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ENVIRONMENTAL RESEARCH IN JAPAN, 1991

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ENVIRONMENTAL RESEARCH IN JAPAN, 1991

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[Selections of summarized reports (pp 1-228) of environmental research conducted in FY91 by the national research institutes of government ministries and agencies.]

CONTENTS

| | |
|--|-------------|
| Foreword | 1 |
| 1. Air Pollution Simulator for Practically Using the Evaluation of Traffic Operational Countermeasures | NPA 2 |
| 2. A Study on Conservation of Coastal Environment in Cold Regions | HDA 3 |
| 3. An Emission Reduction Research for a Small Stationary Gas Turbine Engine : Emission Characteristics with a Methane-Fueled Conventional Combustor and Preliminary Design of a Variable Geometry Lean Premixed Combustor | STA 5 |

| | | |
|--|-----|----|
| 4. Research on Reduction of Airframe Broadband Noise | STA | 7 |
| 5. Development of Analytical System for Monitoring of Organotin in Marine Environmental Samples | STA | 10 |
| 6. Advanced Treatment Technology of Effluents from Food Factories | MF | 12 |
| 7. Behaviours of Organotin Compounds in Marine Aquatic Environments | MHW | 13 |
| 8. Monitoring System of Pollutants from Solid Waste Disposal Site | MHW | 14 |
| 9. A Study on the Reduction of Toxic Substances from Municipal Solid Waste Incinerators | MHW | 15 |
| 10. Development of Monitoring Method for Personal Exposure to Trace Toxic Chemicals in Air | MHW | 18 |
| 11. Formation Mechanism of Mutagenic Compounds on Acidic Particles | MHW | 20 |
| 12. Study on the Behaviors and Safety Assessment of Environmental Pollutants Chemicals in Ambient Water | MHW | 21 |
| 13. Study on Genetic Mutation in Human Cells by Using Shuttle Vector Plasmid | MHW | 23 |
| 14. Studies in the Assessment of Putative Potential Toxicity of Environmental Pollutants at Low Doses Using Culture Systems | MHW | 25 |
| 15. Estimation of Risk to Humans by Extrapolation from Low Doses Animal Data : Toxicokinetic studies | MHW | 27 |
| 16. Safety Assessment of Microorganisms Used for Recombinant DNA Technology | MHW | 30 |

| | | |
|---|------|----|
| 17. Evaluation Methods for Biological Effects of Rare Earth Metals | MHW | 32 |
| 18. Effect of Organochlorine Compounds on the Lung Immunity to Respiratory Pathogens | MHW | 35 |
| 19. Studies on the Influences of Chemical Control on the Target and Non-target Populations with Special Reference to Insecticide Resistant Mechanisms | MHW | 37 |
| 20. Study on Distribution of Metals in Soils in Japan for Evaluation of Environmental Pollution and of Health Effects by Their Utilization in Advanced Industry with Technical Progress | MHW | 39 |
| 21. Studies on Genetic Damage and its Biological Effects by Organochlorine Environmental Pollutants and on their Modification by Nutritional Conditions | MHW | 41 |
| 22. Effect of Environmental Substances on Defense Function in Immuno-deficient Patients | MHW | 42 |
| 23. Development of a Convenient In Vitro Assay to Screen for Substances that Initiate or Enhance the Allergic Reaction to Japanese Cedar Pollen | MHW | 44 |
| 24. Problems Caused by Nitrogenous Pollutants in Domestic Water Use and Their Control | MHW | 46 |
| 25. Technical Development for Ecological Control of Noxious Red Tides | MAFF | 48 |
| 26. Study on the Optimal Allocation Method of Green Resources by the Synthetic Assessment | MAFF | 50 |
| 27. Studies on a New Methodology Using Marine Fish to Evaluate Toxic Effects of Pollutants on Marine Organism | MAFF | 52 |

| | |
|--|---------------|
| 28. Development of Nitrate Removal Techniques in the Shallow Groundwater by using Agricultural Ecosystems | MAFF 54 |
| 29. Studies of Simulation Methods of Suspended Particulates Concentration from Industrial Emissions | MITI 59 |
| 30. Efficient Treatment of Offensive Odors by Using Functional Polymeric Materials and Microorganisms | MITI 61 |
| 31. Emission Control of Volatile Organic Halides by Adsorption | MITI 65 |
| 32. Catalytic Combustion Technique for Reduction of NOx from Small Scale Stationary Sources | MITI 67 |
| 33. Evaluation and Control of SOF from Diesel Engines | MITI 72 |
| 34. Study on the treatment of toxic gases | MITI 74 |
| 35. Study on Hybridized Catalytic System for Diesel NOx Removal | MITI 75 |
| 36. Simultaneous Control Techniques of N ₂ O and NOx from Coal Combustion | MITI 81 |
| 37. Air Pollution Control of Automobile Exhaust Gas in Urban Road Tunnels | MITI 84 |
| 38. Effective Treatment of Hazardous Chemicals by Ecological Control of Activated Sludge | MITI 86 |
| 39. Treatment of Chemicals in Waste-water by Supercritical Fluid | MITI 88 |
| 40. Study on the New Advanced Techniques for Treatment of Waste-water Containing Hazardous Substances from High-technology Industries | MITI 90 |

| | |
|--|----------------|
| 41. Catalytic Oxidation of Refractory Organic Substances | MITI 92 |
| 42. Treatment Technology of Waste Water from Waste Paper Recycling Process | MITI 96 |
| 43. An Advanced Technique for Treatments of Waste Water Containing Organic Materials | MITI 98 |
| 44. Behaviors of Synthetic Organic Compounds in Coastal Environment | MITI 99 |
| 45. Long Range Prediction Model for the Change of Shallow Water Environment for Optimum Industrial Development | MITI 101 |
| 46. Development of New Removal Method of Polluted Sediment in a Coastal Sea | MITI 105 |
| 47. Removal Method of Polluted Lake Sediment | MITI 107 |
| 48. Appropriate Flow Control in the Seto Inland Sea by Topographical Changing Measures for Environmental Enhancement | MITI 109 |
| 49. Evaluation Method of Structures and Purifications of Shoreline Environments | MITI 111 |
| 50. Studies on the Anti-fouling Polymeric Materials | MITI 113 |
| 51. Nitrogen Cycling at Sediment-Water Interface in Coastal Marine Environments | MITI 114 |
| 52. Treatment of Industrial Wastes Containing Mixed Hazardous Organic Compounds | MITI 118 |
| 53. Treatment and Advanced Utilization of Asbestos Waste by Transformation of the Fibrous Form | MITI 120 |
| 54. Research on Waste Treatment of Advanced Technology Products | MITI 122 |

| | |
|---|----------------|
| 55. Microbial Treatment of Natural Rubber and Plastic Waste | MITI126 |
| 56. Control of Structure-borne Noise | MITI132 |
| 57. Psychological and Physiological Measurement of Fluctuating Low Frequency Noise | MITI 134 |
| 58. Outbreak and Propagation Mechanism and Measuring Method of Impulsive Low Frequency Sound | MITI136 |
| 59. Development of Air Monitoring for Individual Components in Suspended Particles | MITI 138 |
| 60. Evaluation and Measuring Method of Source Dust in Consideration of the Relation with SPM | MITI 140 |
| 61. Psychological and Physiological Measurements for Fluctuating Offensive Odors | MITI 142 |
| 62. Rapid Determination Techniques of Pollutants in Groundwater | MITI 146 |
| 63. Structure of Lower Trophic Ecosystem in a Eutrophicated Bay-automated Measurement and Prediction on Plankton Organism Succession | MITI 148 |
| 64. Study on Techniques of Predicting Environmental-related Parameters for Advance Environmental Assessment of Chemical Substances | MITI 151 |
| 65. Study on the Reductive Degradation of Harmful Organic Compounds | MITI 154 |
| 66. Efficiency Improvement Techniques for Evaluation Methods on Exhaust Emission Control system | MT 156 |

| | | |
|--|-----|-----|
| 67. New Technologies to Control NOx Emission from Diesel Engines and their Applicability under Actual Driving Conditions | MT | 158 |
| 68. Study on Reduction of Exhaust Gas Emissions from Marine Diesel Engines | MT | 160 |
| 69. Study on Estimating the change Process of Noxious Liquid Substances in the Ocean | MT | 163 |
| 70. Water Quality Improvement at Coastal Shore of Waterfront Development Area | MT | 164 |
| 71. Development of Low Atmospheric Radar for Studying the Pollutant Transport | MPT | 166 |
| 72. Asbestos Fiber Real-time Monitor Detecting Polarized Scattering Light | MPT | 168 |
| 73. Development of Electrical Treatment System for Oil Mists Dispersed in Factories | ML | 170 |
| 74. Prevention of Uncontrolled Discharge into the Atmosphere of High-Concentration Harmful Gases Mainly Used in Semiconductor Industries | ML | 172 |
| 75. Development of Measuring Method for Concentration of Suspended Fine Particulate Matters under $2\mu\text{m}$ in an Urban Atmosphere | ML | 174 |
| 76. A Study on the Amounts of Exposure to Halogenated Hydrocarbons by Different Routes | ML | 175 |
| 77. On Evaluation of Biological Effects of Chlorinated Hydrocarbons by an Electrophysiological Method | ML | 177 |
| 78. Assessment of Effects of Electromagnetic Field by Biological Monitoring | ML | 179 |

| | | |
|---|----------------|-----|
| 79. Research on Utilization technique of Melted Slag and Incinerated Ash of Sewage Sludge | MC | 180 |
| 80. Study on Research Methods to Clarify Pollution in the Reef Flat Zone in Coral Reef Islands Using Aero-Survey and Space Image | MC | 181 |
| 81. Conservation Methods of Natural Environment in Urban Rivers | MC | 183 |
| 82. Planning Technique for Residential Districts with Full of Amenity and Conserving Natural Environment | MC | 186 |
| 83. The Study on Technology to Reduce the Noise Generated by Construction Machine | MC | 188 |
| 84. Researches on the Method to Evaluate Lotic Environments Based on the Biological Condition of Macrobenthic Invertebrates in Japan | EA | 190 |
| 85. Study on Preservation and Mechanism of the Stabilization of Coral Reef Ecosystem | EA | 193 |
| 86. Regenerable Filter Trap Oxidizer and Oxidation Catalyst System for Diesel Particulate Control | MITI, MT ... | 196 |
| 87. Development of New Wastewater Treatment Technologies for Environmental Water Quality Control | MHW, MC | 200 |
| 88. Prediction of Wind-Driven Currents and Mass Transport in an Enclosed Sea | MITI, MT ... | 202 |
| 89. A Study for the Conservation of the Wetland Ecosystem :Establishment of the Method of Monitoring the Ecosystem and the Countermeasures to the Influence from the Surrounding Agricultural Lands | EA, MAFF ... | 206 |
| 90. Prevention and Control of Wildlife Damage for Crops | EA, ME, MAFF . | 209 |

| | |
|--|-----------------------------|
| 91. Occurrence Mechanism and Prevention of Soil Loss into the Sea from the Agricultural Land in Ryukyu Islands | MAFF, MC ... 217 |
| 92. Diffusion Processes and Monitoring Method of Pollutants Related to High Technology Industries | MITI, MAFF MHW 220 |
| APPENDIX..... | 229 |

Foreword

Needless to say, any effective measures for environmental preservation cannot be promoted without accumulated scientific knowledge. Such environmental knowledge covers various scientific fields, and concerted efforts must be made not only to further research and study in these individual fields but also to promote cooperation among research and study in different fields. Therefore, in promoting these studies, it is necessary to establish a comprehensive and unified research system with close cooperation among research institutes.


The Environment Agency appropriates in a lump sum all the costs of environmental preservation researches and studies to be undertaken by national research institutes as well as all the costs of research and studies commissioned by governmental ministries to promote environmental researches and studies harmoniously.

In F.Y.1991 the Environment Agency appropriated a total of 1,928 million yen for 92 environmental researches and studies undertaken by 45 research institutes of 13 ministries and agencies concerned.

This volume is the compilation of the summarized reports of these researches carried out in F.Y.1991.*

The Agency hopes that this volume will prove helpful to those who are interested in environmental research in Japan.

September 1992



Hotsuma Miyakawa
Director
Environmental Research
and Technology Division
Environment Agency

* This volume does not contain researches undertaken by the National Institute for Environmental Studies, and Universities and their laboratories.

1. Air Pollution Simulator for Practically Using
the Evaluation of Traffic Operational Countermeasures
(FY 1989~1992)

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Traffic Regulation Section, Traffic Division
National Research Institute of Police Science
National Police Agency

In spite of the frequent revision of the regulation criteria of the pollution materials in vehicle emission gas, environmental situation is not sufficiently improved in urban areas, which necessitates further comprehensive countermeasures for the preservation of urban environment from all its aspects not only from the revision of regulation criteria of emission sources but also from the improvement of roads and traffic flows there actually worked for social economical activities.

The countermeasure from the standpoints of improving traffic flow is the most useful ones for its practicality and promptness, but only limited studies have been conducted and no useful outcomes were obtained yet. Therefore, the studies from this aspect is promptly needed.

This study is regarding traffic flow management classified as a traffic countermeasure for the preservation of urban environment, aiming at developing a practical computer simulator that enables to assess beforehand the air pollution reduction effect of various method of traffic control precisely and easily.

In 1989, the tasks in the study carried out were; to transference of a readily developed simulation model into a personal computer, to collect and to sort literatures to be referred to for development of emission model to estimate the quantity of the pollution materials and to develop the emission model.

In 1990, the tasks were; to make clear the relationships between the emission levels and traffic flow by using the data taken in the field study, and to examine the framework of a dispersion model to estimate the pollutant levels at road edges.

In this year 1991, the tasks were; to newly develop the macroscopic simulator being able to deal urban network, based on the MACSTRAN-I model, which is the traffic flow simulation model already developed, and to validate the output of the simulator by comparing with field data taken at the Ginza network in Tokyo.

2. A Study on Conservation of Coastal Environment in Cold Regions
(FY 1989 ~1993)

Tomoyuki Takeuchi, Takahiro Johnishi, Jun-ichi Maeda

Yasuhiro Ohmori and Jin Satoh

Civil Engineering Research Institute

Hokkaido Development Bureau

In recent years, there are abnormal outbreaks of phytoplankton bloom in eastern coast of Hokkaido. However generative mechanism of the phenomenon is not clarified. In order to conserve coastal environment off Tokachi, it is necessary to take properties of current, water quality, seabed material and etc. into consideration.

The purpose of this study is to establish guidelines for environmental evaluation, with investigation on physical and chemical conditions of coastal areas and surrounding ones. Observations of current, vertical temperature profile, water quality and seabed material at three areas (Ohtsu, Hamataiki and Hiroo) off Tokachi were carried out at September, 1991. Observations of water level, water quality and bottom material of Lake Chobushi, Lake Oikamanai and Lake Yudo along Tokachi coast were carried out in autumn, 1991.

1. Pollution load from Tokachi river

Pollution load from Tokachi river are evaluated by three factors of discharge from Tokachi river, the rate of land utilization and quantity of suspended solids.

2. Properties of hydraulics and water quality

(1) Currents

Predominant direction of surface current is along contour line. However bottom current is irregular and locally distinct because of topography. Evident changes of current and water temperature profiles are caused by tidal changes.

(2) Vertical distribution of water temperature

Difference of water temperature between sea surface and bottom is up to 4-5°C when sea condition was calm, however, is little because of vertical mixture when sea condition was rough.

(3) Water quality and seabed materials

Water quality of Tokachi river have the greatest influence on water quality off Ohtsu, in comparison with other coastal areas. Seabed off Tokachi is sandy with over 80% fine sand and about 10% silt. However, seabed of many parts off Hiroo is high organic with about 50% clay.

(4) Discharge from Coastal lakes

Several sudden drawdowns from coastal lakes are occurred every year. Discharge from coastal lakes is as much as 100-200 m³/s to be similar to Tokachi river. In order to estimate long term tendency of water quality off Tokachi, it is necessary to take pollution load from coastal lakes into consideration.

3. An Emission Reduction Research for a Small Stationary Gas Turbine
Engine: Emission Characteristics with a Methane-Fueled
Conventional Combustor and Preliminary Design of a Variable
Geometry Lean Premixed Combustor
(FY 1990 - 1993)

Hideshi Yamada, Kazuo Shimodaira, Shigeru Hayashi,
Takashi Saito, and Shouji Horiuchi
National Aerospace Laboratory, Science Technology Agency

1. Preliminary design study of a variable geometry can combustor

In this research program the lean premixed low-NO_x combustion concept is to be evaluated by using a 250-kW gas turbine engine. In FY 1991 a combustor model (Fig. 1) was designed and fabricated to evaluate a variable geometry mechanism. Rotatable ring-shaped air flow regulating valves were used to vary the opening areas of the primary air and dilution air passages. Servo-motors were used to actuate the valves. The effective flow coefficients of these air passages were determined as a function of the valve opening.

The main fuel is premixed with combustion air upstream of the combustion region and the pilot fuel is injected from a multi-hole nozzle placed coaxially with a swirler. The equivalence ratio in the combustion region is controlled in a narrow range for lower NO_x emissions and acceptable combustion efficiencies by regulating the combustion air and fuel flow rates. Tests on flame stability, and combustion and emission characteristics of the combustor and the operation tests of the controller are to be conducted in FY 1992.

2. Evaluation of the emission characteristics with a conventional combustor

Emission characteristics of the gas turbine engine have evaluated with a conventional rich-primary zone combustor for natural gas (methane) and kerosine. The emission index for NO_x and combustion efficiency are plotted against load in Fig. 2. The emission index for NO_x at the full load condition with methane was about 7 gNO₂/kg Fuel, being lower than the level obtained with kerosine. This index was by 20% lower than the regulated standard provided for in the Air Quality Law in Japan (70 ppm at 16% oxygen concentration), but is more than two times of the regulation standard for the Tokyo Metropolitan District (100 ppm at 0% oxygen concentration).

The effect of an increase of the primary air flow on NO_x emissions and combustion efficiency was also investigated by plugging four of the eight dilution air holes. Emission index for NO_x was found to decrease by 15%-20% depending on the load. At the lower load condition combustion efficiency was lower than that with the original combustor showing combustion efficiency greater than 99%. Reduction was more significant with methane: Combustion efficiency was less than 99% at loads less than the half load.

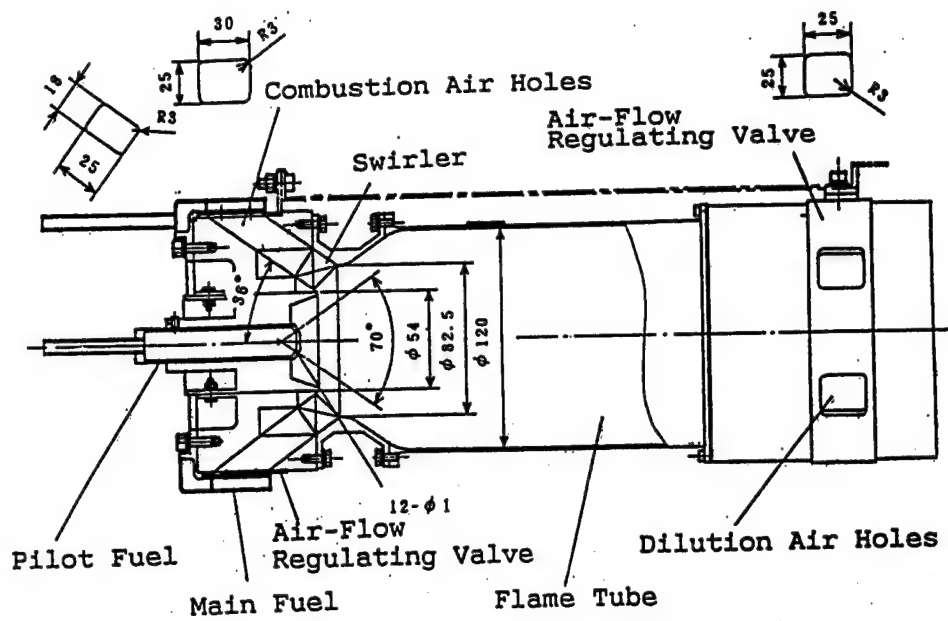


Fig. 1. Variable geometry combustor model

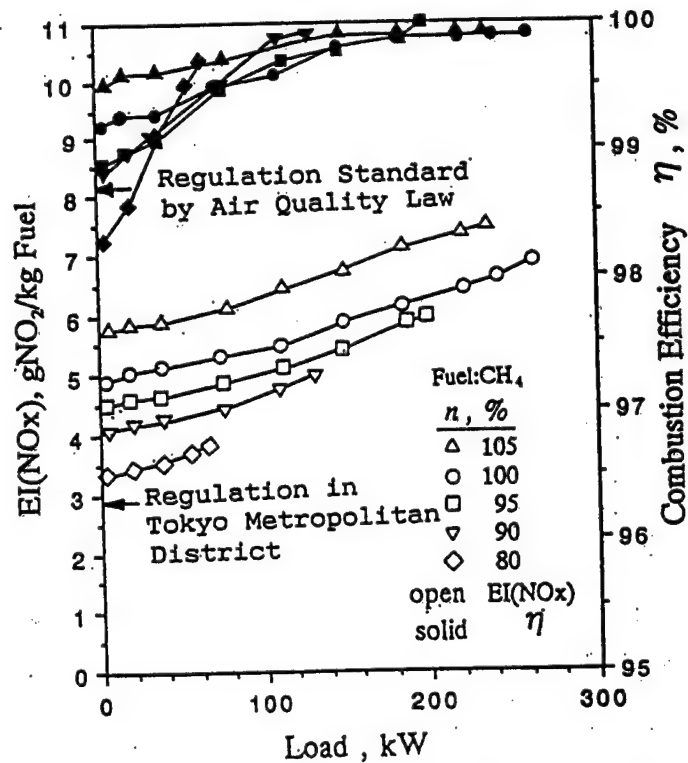


Fig. 2. Variation of emission index for NOx and combustion efficiency with load for different speed n .

4. Research on Reduction of Airframe Broadband Noise

(FY 1990~1992)

Hideo Nishiwaki, Katsumi Takeda, Hiroshi Kobayashi

Mitsuo Gomi and Minoru Watanabe

Thermofluid Dynamics Div.

National Aerospace Laboratory, Science and Technology Agency

Aircraft noise research and abatement technology has been mainly concerned with narrowband noise, for example, engine noise and some airframe noise generated by the extended landing gear, well doors and wheels cavities. However, recently airframe broadband noise from the surfaces or the edges of wings and fuselage is becoming a significant contributor to the overall airframe noise, especially under landing conditions.

The main objective of the current experimental study is to determine the characteristics of the airframe broadband noise and to propose less noisy fuselage configurations.

This year as a second step to the current research, an experiment concerning the relationship between sound pressure levels of airframe broadband noise and flow speed were conducted. In this regard, a rotating drum test facility was utilized to experimentally determine the relationship between airframe noise and flow speed. This method has the advantage of a lower background noise level than typical wind tunnel experiments. Overall sound pressure level data from the surface of the rotating drum were acquired between rotational velocities of 40 and 164 m/s.

The test facility is shown in Figure 1. Sound pressure data were measured at a distance of 2.0 m in front of the rotating drum. The results are shown in Figure 2. In this case, the overall sound pressure level is proportional to the sixth power of the rotational velocity when the velocity is between 116 and 164 m/s. It is proportional to the fifth power for velocities between 70 and 116 m/s and the fourth power for velocities between 40 and 70 m/s.

A second wind tunnel experiment for airframe broadband noise abatement was also conducted using a riblet surface. The surface shape was designed using information from several references concerning viscous drag reduction techniques. The references reported that a surface drag reduction of 7 to 8 percent could be achieved using a proper riblet shape. It

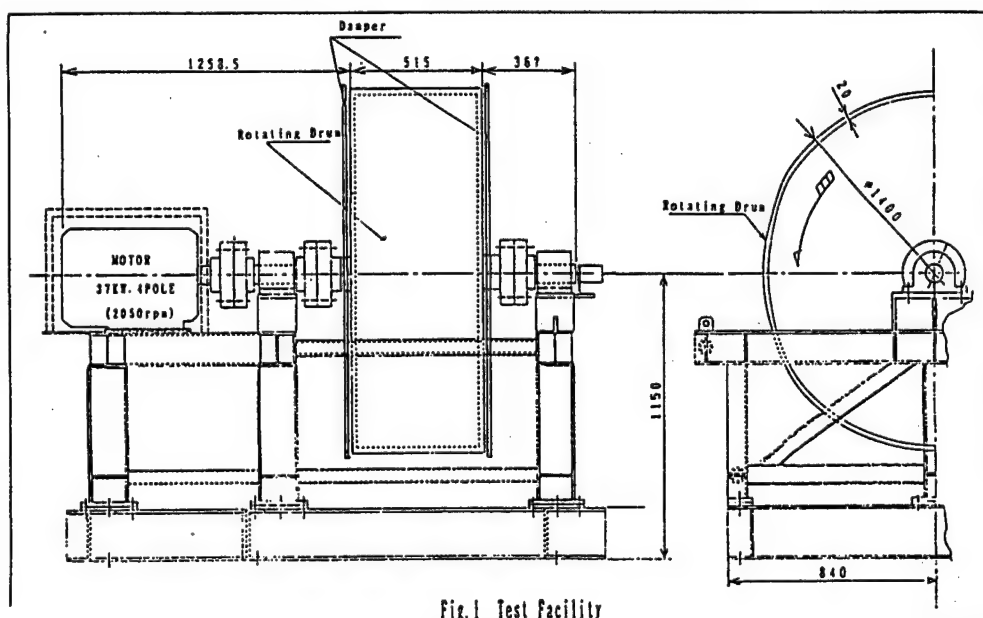
was hypothesized that in these cases the sound pressure might be reduced also. However, accurate measurements using flush-mounted microphones on the riblet surface, or using turbulent screen type microphones inserted squarely to the surrounding four plates revealed that the data was not significantly different than the same experiments with a smooth surface.

It was also hypothesized that the background noise level was high in comparison with airframe broadband noise scattered from a riblet or smooth surface. Figure 3 presents some sample data.

A second wind tunnel experiment was also conducted using a riblet surface, but the data was not significantly different than the same experiment with a smooth surface. Therefore, a significant decrease in the sound pressure level could not be achieved by this method.

In the next year, the study of broadband noise will continue and be expanded to consider edge noise by using the rotating drum test facility.

Reference : M.J.Walsh "Turbulent Boundary Layer Drag Reduction Using Riblets" AIAA-82-0169, 1982.



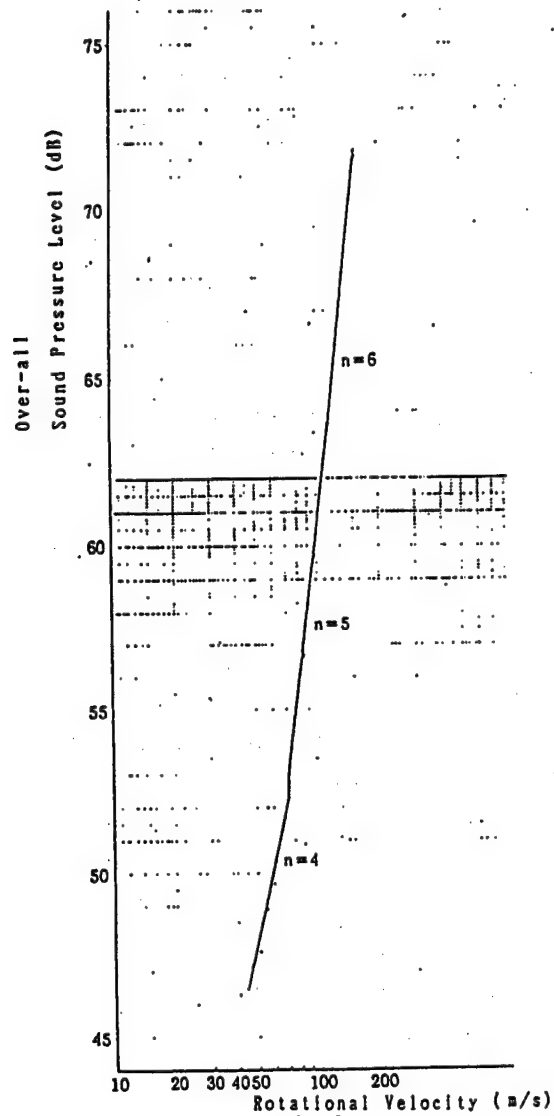


Fig. 2 The Relation between Sound Pressure and Velocity

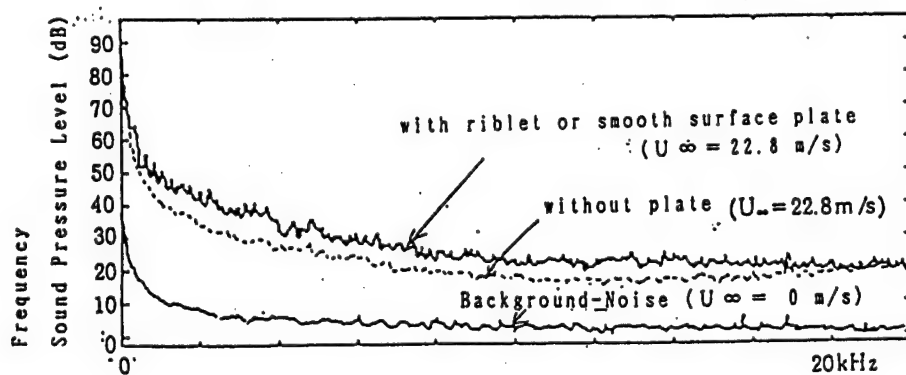


Fig. 3 The Level of Airframe Noise

5. Development of Analytical System for Monitoring of Organotin in Marine Environmental Samples
(FY 1991-1996)

Haruno Okochi, Muneyuki Kohri, Koichi Sato and Kunikazu Ide
National Research Institute for Metals
Science and Technology Agency

1. Determination of Tin (IV) and organotin species in sea water by inductively coupled plasma mass spectrometry after hydride generation.

In order to monitor ultra-trace of organotin compounds in sea water, a high sensitive analytical method have been investigated. Inductively coupled plasma mass spectrometry (ICP-MS) has been used as a high sensitive detector. Organotin compounds are volatilized from sea water by hydride generation, trapped on a chromatographic packing material, separated on the basis of differing boiling points, and introduced into the ICP plasma. The species under investigation are triphenyltin (TPT), diphenyltin (DPT), monophenyltin (MPT), tributyltin (TBT), dibutyltin (DBT), monobutyltin (MBT) and inorganic tin. An artificial sea water was used for the investigation. The optimum temperatures for volatilization from solutions have been examined and all the organotin compounds hydrides give the highest signals at 60-70°C. The sensitivities increase 3-5 times more than those at a room temperature. The analytical procedure is as follows. 100ml of sea waters are placed into a reaction flask and acidified to pH 2 with 2M HNO₃. The bubble of He through the sample for 3 min to strip O₂ from the solution. 2ml of 1% sodium tetrahydroborate are injected over a period of 20s into the solution of 60-70°C. Generating hydrides are trapped into a cold trap packed with chromosorb GAW-DMCS. The collected hydrides volatilize in

Table 1 Detection limits and sensitivity of tin and six species of organotin compounds

| Tin species | Detection limit ^{a)} | Sensitivity ^{b)} |
|-------------|-------------------------------|---------------------------|
| Tin | 0.03 | 5.50×10^4 |
| MPT | 0.21 | 1.09×10^4 |
| DPT | 0.43 | 5.80×10^2 |
| TPT | 1.88 | 7.57×10^2 |
| MBT | 0.13 | 1.55×10^4 |
| DBT | 0.72 | 1.16×10^3 |
| TBT | 5.60 | 1.70×10^2 |

a) unit : ng · l⁻¹

b) unit : cps · ng⁻¹ · l

Table 2 Operating parameters

| Atomic absorption spectrophotometer | | | |
|-------------------------------------|-------------|-----------------|---------|
| Light source | HCL at 15mA | | |
| Wavelength | 286.3nm | | |
| Spectral band-width | 0.7nm | | |
| Integration time | 8s | | |
| Graphite furnace ^{a)} | | | |
| Step | Temp.(°C) | Ramp(s) | Hold(s) |
| Drying | 130 | 20 | 20 |
| Ashing | 1050 | 20 | 20 |
| Atomizing ^{b)} | 2400 | 0 ^{c)} | 8 |
| Cleaning | 2650 | 1 | 4 |

a) 20μl sample injection by AS-60 autosampler

b) Purge gas stop

c) Maximum power mode(2000°C · s⁻¹)

the order of their boiling points by elevating the temperature of the trap. The hydrides are introduced into the ICP-MS. The detection limits and sensitivity of tin (IV) and six species of organotin compounds are shown in Table 1.

2. Determination of total tin in marine sediments by graphite furnace atomic absorption spectrometry.

A method for the determination of "total" tin in sediments by graphite furnace atomic absorption spectrometry have been developed. Samples are decomposed with HNO_3 , HF , and HClO_4 . The solutions are vaporized to dryness and the residues are dissolved with HNO_3 . The stabilized temperature platform furnace technique is applied. The operating parameters of atomic absorption spectrometry is shown in Table 2. Nickel is used for a matrix modifier. There is no effect of diverse elements at least up to Fe (10% in a sample), Ca (5%), Mg (3%), K (1%), Mn (1%), P (1%), and Ti (1%). Al is tolerated up to 10%, but 15% of Al gives -5% error. Accordingly, Al equivalent to 20% in a sample is added to the standard solutions for preparation of calibration curves. Limit of detection (3σ) is 54pg, that is, 0.27ppm in the case of 0.5g sampling.

3. X-ray fluorescence analysis of marine sediments by glass bead technique.

X-ray fluorescence analysis of sediments has been investigated. Analytical elements are Si, Ti, Al, Fe, Mn, Mg, Ca, K and P of main constituents. The sample preparation methods are compared between a glass bead technique and bliquet one. Consequently, bead samples are prepared in a small dilution rate of 1.17 using 3g of a sample. Preoxidation of organic materials in sediments is required. The matrix effects are corrected by the theoretical alpha coefficients method. TG-DTA curve of a sediment is shown in Fig. 1.

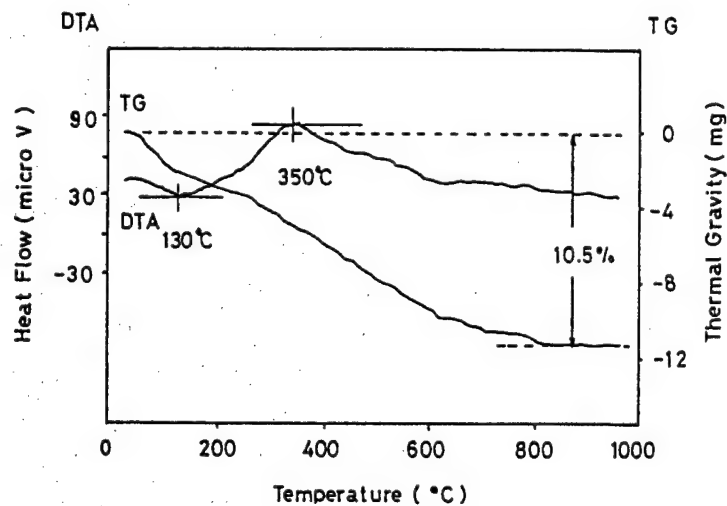


Fig.1 TG-DTA curve for NIST 1646.

Weight sample : 50mg, elevating temperature rate : $20^{\circ}\text{C} \cdot \text{min}^{-1}$.

6. Advanced Treatment Technology of Effluents from Food Factories (Part III)

(FY 1989-1992)

Takaji Obata, Yuzuru Imura, Haruyuki Iefuji and Hitoshi Shimoi

National Research Institute of Brewing

National Tax Administration, Ministry of Finance

The wastewater discharged from *shochu* distillery, especially from *imo-shochu* (sweet potato-*shochu*) distillery, contains a large amount of insoluble solid, which is composed of cellulose and hemicellulose. The insoluble solid, which causes the viscosity of the wastewater to be much higher, results in the difficulty of the advanced treatment. Then the development of simple and inexpensive method of solid-fluid separation for the wastewater was carried out.

In this paper, to develop new method of solid-liquid separation using the microorganism cell as aggregation reagent, we screened microorganisms having aggregation-accelerating ability of the insoluble solid using the wastewater as medium, and then isolated a strain, MIII, from soil. After incubated in YPD medium, the cell of MIII were added to the wastewater at final cell density of 1×10^7 cells/ml. Immediately after gentle stirring, strong aggregation occurred. The resulting flocculi were able to be removed easily by filtration using a cloth of large meshes like gauze as filter. No other insoluble solid than yeast cell was observed in the obtained filtrate.

We determined morphological and physiological characteristics of MIII. From the results, MIII was identified as a kind of *Geotrichum* yeast, *Trichosporon* sp.. This strain is able to grow at optimum temperature of 28 °C, pH 5 and in vitamin-free medium, but not at 37°C, and assimilate galactose, D-xylose, ribitol, D-mannitol and succinic acid, but not sucrose, maltose, cellobiose, trehalose, lactose, raffinose, soluble starch, L-alabinose, D-ribose, L-rhamnose, erythritol, citric acid and inositol as a sole carbon source. From these results, it is suggested that MIII can be used for secondary treatment to remove COD in the filtrate.

The cells of MIII also had aggregation-accelerating ability of following insoluble solids: filter cellulose, tomato juice, pulp wastewater, talcum powder, active charcoal, Avicel, cellulose powder and kaolinite. These results suggested that MIII can be extensively used in the treatment of wastewater discharged from various food industries.

In order to elucidate the mechanism of the aggregation with the cell of MIII. We treated the cell with various detergents or proteinase K, and then estimated the aggregation-accelerating ability of the resulting cells. As results, no ability against the solid in the wastewater and filter cellulose was observed in the cell treated with SDS or proteinase K. On the other hand, the treatment with some kinds of detergent CTAB, Tween 20 and TritonX-100 causes the ability against talcum powder, active charcoal and kaolinite to be much lower. These results suggested that the aggregation-accelerating ability against the solid in wastewater or cellulose is responsible to the protein on the surface of the cell.

This protein may be stable in high temperature above 90°C, because the ability is effective in the hot wastewater discharged from *shochu* distillery immediately after distillation. Also, the ability was independent on the cell age of MIII. This characteristics can make the treatment to be much easier.

In further studies, we will establish a advanced treatment system involving this system for wastewater from food industries.

7. Behaviours of Organotin Compounds in Marine Aquatic Environments
(FY 1991~1993)

Yukio Saito, Takashi Suzuki, Makoto Miyahara, Rieko Matsuda, and
Satoshi Takatsuki

National Institute of Hygienic Sciences

Molecular species of organotin compounds derived from tri-n-butyltin compounds (Bu_3Sn^+) were investigated at the ppb level in marine products. After being divided into flesh, eggs and liver, the samples were homogenized and extracted. After purification, the extracts were alkylated by methylmagnesium bromide, and the resulting tetrasubstituted tin compounds were identified by gas-liquid chromatography/mass spectrometry/selective ion monitoring (GC/MS/SIM), and quantified by GC/MS/SIM, using authentic specimens. Analysis of fish samples purchased in several retail stores showed the presence of 13 organotin compounds, including triphenyltin compounds. The products hydroxylated and carboxylated at a butyl moiety of Bu_3Sn^+ were found in liver, eggs and flesh. The products hydroxylated at an alkyl side chain of $\text{Bu}_2\text{Sn}^{2+}$ were mainly found in liver. A carboxylated products was found in liver of only one species.

And also determination of Bu_3Sn^+ and $\text{Bu}_2\text{Sn}^{2+}$ in yellowtails at various growth stages was carried out. Results of analysis showed that $\text{Bu}_2\text{Sn}^{2+}$ was present at the highest levels in liver followed by red muscle and then white muscle. On the other hand Bu_3Sn^+ was present in liver and red muscle in the similar levels and at the lowest levels in white muscle. Wakashi and Inada contained more Bu_3Sn^+ than $\text{Bu}_2\text{Sn}^{2+}$ in both the liver and white muscles but the liver of Hamachi contained $\text{Bu}_2\text{Sn}^{2+}$ rather than Bu_3Sn^+ . Little $\text{Bu}_2\text{Sn}^{2+}$ was found in the white muscle of Hamachi. The difference in $\text{Bu}_2\text{Sn}^{2+}/\text{Bu}_3\text{Sn}^+$ ratio between Wakashi or Inada and Hamachi might be attributed to increased metabolic ability of fish according to the age of fish.

8. Monitoring System of Pollutants from Solid Waste Disposal Site

(FY 1990~1994)

The Institute of Public Health
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Kyoto University
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Tsukuba University
Norio TASE

The solid waste disposal site has many issues to be solved in order to properly treat solid wastes which recently increase in volume and become to have various components. Especially we don't necessarily have regular solution methods, for example, about estimating the long term environmental effects from the site, and for consensus making with the recountermeasures of accidental pollution.

The purpose of this studies is to reasonably integrate monitoring systems related with the landfill disposal site considering characteristics of solid waste, the structure and classification of the site, location conditions of the site, the actual state of environmental pollution by accident caused from the site and others.

In the second year of scheduled five years, the following four items were studied.

- (1) Investigation by using the disposal site model on the detection system for leakage from the seepage control work of the site,
- (2) Planning of optimal location of sampling wells for environmental monitoring of groundwater pollution,
- (3) Application of TDR(Time Domain Reflectometry) method to the electromagnetic determination of soil water content in order to predict the movement of hazardous substances through groundwater around the site, and
- (4) Field investigation on the actual state of vertical distribution of heavy metals in the disposal site.

9. A Study on the Reduction of Toxic Substances from
Municipal Solid Waste Incinerators
(FY 1990-1992)

Masaru Tanaka, Masanobu Miyazaki and Ikuo Watanabe
The Institute of Public Health

Introduction

There are about 1,900 municipal solid waste incinerators in Japan and most of them are mechanized batch type incinerators which are operated intermittently as their start up and shut down in every morning and evening, respectively. It is known that during such unstable operations, they tend to emit unburnt organic compounds at high level under lower furnace temperature. With the characteristics of dioxins generation, they might emit a large quantity of dioxins even in the start up, shut down and night time period except day time steady operation. Therefore, reduction of emission of dioxins under these unstable operations is also important and effective in order to reduce a whole day emission of dioxins from the mechanized batch incinerators.

Experiment

In this respect, we carried out a series of investigations to find ways to reduce the total daily emission of dioxins at a full-scale MSW incinerator. This incineration plant has two furnaces with capacity of 10 ton/8hrs, which consist of cooling water injection, dry HCl removal systems and dry electrostatic precipitators. To ensure good combustion at the furnace, an additional secondary blower was installed. The outlet of the electrostatic precipitator (EP) was selected as sampling point for gas analysis.

Results

Total dioxins concentration at the outlet of EP and total daily emission of dioxins are shown in Figure 1 and 2. It can be recognized from these data that the quantity of dioxins emitted in the unstable processes was 91% of those emitted in a whole day containing stock-fire operation. It can be also found that generation of dioxins in the unstable processes was suppressed by changing stock-fire

operation for burn-out operation and then total daily emission of dioxins at the plant was reduced to 34%.

Total dioxins concentration, CO concentration, chlorobenzenes (CBs) concentration, chlorophenols (CPs) concentration and O₂ concentration at the outlet of EP in the stable processes are shown in Table 1. By comparison of the data before installation of an additional secondary blower with the data after installation of the blower, concentration of total dioxins, CO, CBs and CPs decreased and that of O₂ increased. Decrease of CO concentration and increase of O₂ concentration indicate better combustion was established by the installation of the additional blower. Decrease of CBs and CPs indicates that the combustion of the hydrocarbon proceeded and then the generation of CBs and CPs, which are regarded as precursors of dioxins, were suppressed.

Conclusions

We carried investigations to find how to reduce the total daily emission of dioxins. From our experimental results at the full-scale mechanized batch incineration plant, we can conclude that the quantity of dioxins emitted under unstable processes such as shut down and night time period can be reduced by changing stock-fire operation for burn-out operation and the quantity of dioxins under stable processes can be reduced by installation of an additional secondary blower.

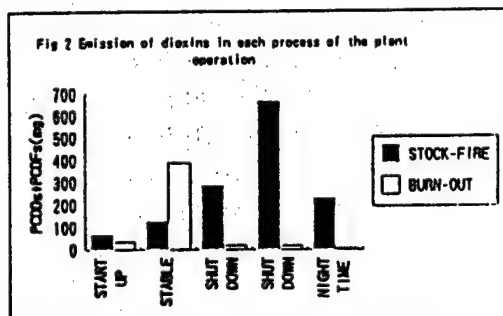
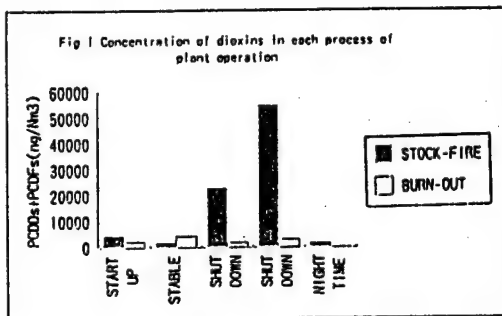


Table 1. Effect of installation of an additional secondary blower on the concentration of dioxins, CO, CBs and CPs in the stable process

| | without the additional blower | without the additional blower | with the additional blower | with the additional blower |
|--------------------------------------|-------------------------------------|-------------------------------------|----------------------------------|----------------------------------|
| PCDDs+PCDFs (ng/Nm ³) | 6900 | 8600 | 1810 | 4500 |
| CO (ppm) | 1560 | 430 | 219 | 246 |
| CBs (μ g/Nm ³) | 96 | 100 | 43 | 25 |
| CPs (μ g/Nm ³) | 130 | 290 | 440 | 100 |
| O ₂ (%) | 10.4 | 13.9 | 14.7 | 12.5 |

10. Development of Monitoring Methods for Personal Exposure to
Trace Toxic Chemicals in Air
(FY 1991~1994)

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Health effects of long-term exposure to trace toxic chemicals in air is attracting attention. Especially, in relation to increase of lung cancer, various efforts have been started for exposure assessment of carcinogens/mutagens in air. It is well known that human exposure to air pollutants cannot be evaluated only based on the results of ambient air monitoring. Survey on personal exposure and indoor pollution, which is combined with questionnaire survey on indoor/outdoor emission sources, activity records, etc., seems to be effective for accurate/detailed evaluation of human exposure including elucidation of pathway/primary factors of exposure, analysis of exposure - lifestyle relationship, characterization of high-risk group, etc. However, except for some gaseous pollutants, e.g., NO_2 , it is not easy to carry out such survey because of difficulties in monitoring methods such as personal sampling device, ultra-trace analysis, evaluation of complex mixture and unknown toxic chemicals, etc. Therefore, for accurate/detailed evaluation of human exposure to trace toxic chemicals in air, following researches on the development of monitoring methods for personal exposure have been carried out:

Personal mini-pump (500g including battery, 1 ~ 1.5 l/min constant flow over 24 hours) and impactor - filter holder device (50% cut-off diameter = $3\mu\text{m}$ at 1 l/min) have been tested in small-scale personal exposure monitoring of PAHs and mutagens. They showed good performances and were useful for the survey. Most of PAHs and direct mutagens (>90%) were found from fine (respiratory) particulates.

Basic investigation has been performed for the development of personal exposure monitoring method for volatile organic halogenated solvents. The method was constructed from a) sampling by passive sampler containing Tenax TA, b) automatic thermal desorption, and c) GC/MS analysis. It has been confirmed that the method is applicable to sub-ppb ~ ppb level measurement based on 24 hour sampling.

For accurate/detailed evaluation of air pollution/human exposure of PAHs, a comprehensive survey on indoor/outdoor pollution and personal exposure was planned. All samples were collected by personal mini-pumps, PAHs were analyzed by using column concentration HPLC/spectrofluorometric detection, questionnaires were used to get information on activity pattern,

indoor/outdoor emission sources, ventilation, etc. A small scale survey was carried out, and the method was useful/effective to understand air pollution/human exposure of PAHs.

For accurate/detailed evaluation of air pollution/human exposure of nitro-PAHs, a comprehensive survey, which is similar to that on PAHs, was planned. A small scale survey was carried out, and the method was useful/effective to understand air pollution/human exposure of nitro-PAHs.

Ultramicro forward-mutation method has been developed for the measurement of mutagenicity of small amount of airborne particulates. The method was sensitive, and was successfully applied to a) personal exposure samples collected by personal mini-pumps, and b) every 2 hour indoor samples for mutagenicity variation monitoring.

Deposition ratio of particulate PAHs and mutagens to respiratory organs has been investigated. Particulates in expiration were collected by a sampling train which was constructed from Hans-Rudolph mask, filter holder and respirometer. PAH contents and mutagenicity of the expiration samples were apparently reduced from those of corresponding indoor (inhaled air) samples. Deposition ratios calculated based on these values were about 60% for PAHs and were about 50% for direct mutagens.

11. Formation Mechanism of Mutagenic Compounds on Acidic Particles (FY 1989 - 1991)

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The Institute of Public Health

In order to clarify the formation mechanism of mutagenic compounds on acidic particles, two photochemical experiments with high-pressure mercury arc were carried out: aqueous phase formation of sulfuric and nitric acid and heterogeneous photonitration of pyrene and fluoranthene with nitrogen dioxide in the absence and presence of sulfur dioxide in these different atmosphere, nitrogen, oxygen, and purified air.

The kinetics of sulfite photooxidation for two pH ranges were determined:

$$\begin{aligned} -d[S(IV)]/dt &= k_p^{(1)} [S(IV)]^{1/2} [Fe(III)] [H^+]^{-1/2} \text{ for pH } 1-3.2, \text{ and} \\ -d[S(IV)]/dt &= k_p^{(2)} [S(IV)]^{1/2} [Fe(III)] [H^+]^{-1/10} \text{ for pH } 3.2-5.5. \end{aligned}$$

Experiments with actual solar radiation suggested that the oxidation prevailed low concentrations of atmospheric sulfur dioxide. The kinetics of thermal oxidation of nitrite by ozone was determined to show oxidation mechanism including nucleophilic addition of ozone with either nitrite ion or nitrous acid.

Several mutagenic nitro derivatives of pyrene and fluoranthene, both of which are typically contained in diesel engine exhaust gas, were identified as major products of photonitration of the above two polycyclic aromatic hydrocarbons in the presence of nitrogen dioxide: 1-, 2-, and 4-nitropyrene, 1,3-, 1,6-, and 1,8-dinitropyrene, and 2-, and 3-nitrofluoranthene. Among these mutagens, neither 2-nitropyrene nor 2-nitrofluoranthene has been detected in the diesel engine exhaust whereas both are commonly observed in airborne particles. These nitropyrenes were found to be extremely high potent mutagens, two orders of magnitude more mutagenic than benzo(a)pyrene. The yield increased in the order to nitrogen, air, and oxygen for the reaction atmosphere, and the formation of these mutagenic nitro compounds was enhanced with addition of sulfur dioxide, which implied that ozone and/or sulfuric acid would play important roles in the nitration.

Our experiments would explain the formation mechanism of highly mutagenic compounds contained in particulate matter which experienced long-range transport: strong acids are first formed in the water film on the particle surface, and nitrogen dioxides are dissolved into this acidic solution to react, in the presence of solar radiation and pollutant gases of sulfur dioxide and ozone, with organic compounds in the particle to yield high potent mutagens such as 2-nitropyrene nor 2-nitrofluoranthene.

12. Study on the Behaviors and Safety Assessment
of Environmental Pollutants Chemicals in Ambient Water
(FY1989-1991)

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Fumio NAKAMURA, Masanori ANDO, Tasuku KAMEI, Hideo SASANO,
Yuichi OHKUBO, Hiroyuki KONDO, Takako AIZAWA, Hiroo TAKAGI,
Masao SAITOH, Tsutomu OOKUBO, Akira SHYOJI,
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Study Group on the Behaviors and Safety Assessment of Environment Pollutants
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The amount of synthetic chemicals which are used not only in industry and agriculture but also in domestic housing have been increasing year by year. The consumption of newly developed chemicals causes environmental pollution such as the occurrence of synthetic chemicals in drinking water. Among them, pesticides should be given a priority to assess and manage the health risks because of its hazardous potentials. Therefore a comprehensive research project has been started in order to make clear the behaviors of pesticides and their degenerates in ambient eswater and water purification process since 1989. The results of this study are summarized as in follows.

The amount of pesticides applied to agriculture in the selected nine area have been surveyed. The kinds of pesticides used in were largely were different from area to area, and also different from yearly to year even in a same area. Therefore we should implement the areal survey on the application programme of pesticides in advance so as to set an appropriate field monitoring programme.

A new analytical method of a simple pretreatment and quantitative analysis by a single-ion monitoring method of GC/MS as well as HPLC have been developed to analyze pesticides in water samples.

Eleven kinds of pesticides, sixteen insecticides and seventeen herbicides were identified from river water which is used as a drinking water source. The runoff rate of pesticides applied into a paddy rice field was different from each other depending on the kinds of pesticides. It is found that the runoff mechanism of pesticides can be simulated by a survey in small test field or in a laboratory.

The degradation of selected pesticides in an ambient water body and also in water purification processes such as chlorination and ozonation have been studied. A number of by-products such as oxon, chloro-oxon, chloro-toluen, halogenated carboxylic acid and other organic substances were identified from organic phosphates and other kinds of pesticides. Some of them showed mutagenicity in *Salmonella thyphirium* strains.

The conventional water purification system composed of coagulation, sedimentation and sand filtration processes can not be anticipated to have its potential to remove pesticides in raw water. However, 50ppm of powdered carbon application could be a countermeasure to reduce pesticides concentration of up to about 5 times of tentative drinking water quality standards. But DEP and other pesticides having a high solubility in water are difficult to be removed by that amount of powdered activated carbon.

The advanced water purification system composed of the conventional water purification system plus ozonation and granular activated carbon filtration can be anticipated to have its potential to remove most of pesticides excluding those having a high solubility such as simazine.

13. Study on Genetic Mutation in Human Cells by Using Shuttle Vector Plasmid

(FY 1987~1891)

The Institute of Public Health

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The Institute of Hygienic Sciences

Hiroshi Mizusawa

Numerous mutagenic agents are known to interact with DNA, but the molecular mechanisms, by which these agents may cause mutations in mammalian cells, are not well understood. The analysis of mutations in mammalian cells has been hampered by the lack of simple genetic systems. The purpose of this study is to develop the simple method to analyze genetic mutations by environmental pollutants in human cells. For this purpose, we have used shuttle vector plasmid that can replicate in both mammalian cells and bacterial cells. The shuttle vector plasmid contains the *supF* suppressor tRNA gene from *Escherichia Coli* to provide a selectable gene for mutation analysis.

In this study, we analyzed the mutational spectrum induced by three different alkylating agents by DNA sequencing. The shuttle vector was treated *in vitro* with three kinds of alkyl nitrosourea; methyl nitrosourea (MNU), ethyl nitrosourea (ENU) and propyl nitrosourea (PNU), and three series of mutants were analyzed by DNA sequencing. The mutational spectrum appears to be different among three nitrosourea-induced mutations. In MNU-induced mutations, base substitutions were found to be about 75%, and deletions and insertions were 19% and 7%, respectively. 84% of the base substitutions were G·C → A·T transitions. In three alkyl nitrosourea-induced mutations, the majority (80%) of the mutations were G·C → A·T transition type base substitutions. PNU-induced mutations only showed base substitutions and among them 36% were G·C → T·A transversion. As to the distribution of the mutations, more than half of the base alterations were found in the stem region of the folded structure of tRNA. However, single base substitution mutations have been identified at all the four arm regions of the tRNA molecule: TΨC region, D region, anticodon region, and acceptor region. These base substitutions within four regions are likely to lead to inactivation of the *supF* tRNA gene function. These alteration sites are seemed to be involved in specific interactions with the tRNA synthetase or ribosomes or in codon recognition. Although there is only one chain in a tRNA molecule, a majority of the bases are hydrogen-bonded to each other. Hairpin folds bring bases on the same chain into a double-helical arrangement where short stretches of nucleotides are complementary to one another. By the importance of tertiary interactions of tRNA molecule, the *supF* gene has proven to be a particularly good mutagenesis marker, and the shuttle vector plasmid with *supF* gene provides a very useful tool for investigating the mutagenesis in the molecular level. An advantage of the *supF* gene as a selectable gene for mutation analysis is that all types of mutations can be identified and that the small size of the *supF* gene permits rapid sequencing of the entire gene. Next, we assessed the genetic effects of environmental pollutants and active oxygens by using the *supF* tRNA system. There is currently interest in the biological effects of environmental pollutants: trichloroethylene, tetrachloroethylene, tributyltin, organic

mercury compounds; methylmercury(II) chloride, ethylmercury(II) chloride, phenylmercuric acetate, and active oxygens. As active oxygens, hydrogen peroxide and superoxide were examined and superoxide was generated by hypoxanthine - xanthine oxidase. Among these substances, superoxide was relatively effective but the others showed negligible effects. In this study, we also constructed a shuttle vector pZBPVneo which is designed as a shuttle vector for stable, extrachromosomal mutation analysis in mammalian cells. pZBPVneo carries the genome of bovine papillomavirus (BPV), which allows episomal replication of this vector in mammalian cells. pZBPVneo also carries the part of pZ189, which contains *supF* tRNA gene, origin of replication from SV40 virus, the pBR327 origin of replication in bacteria, the *amp^r* gene and a copy of the bacterial neomycin resistance gene (*neo^r*) for a selectable marker, which help to maintain episomal replication of the shuttle vector in mammalian cells. For these reasons, pZBPVneo should be useful for characterization of mutations in mammalian cells. Further analysis of the mutations in tRNA gene may lead to a better understanding not only of the molecular mechanisms of genetic mutations in mammalian cells but also of the structure and function of tRNA molecules.

14. Studies in the Assessment of Putative Potential
Toxicity of Environmental Pollutants at Low Dose
Using Culture Systems (FY 1987-1991)

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Effects of dibenzofuran (DF), and 2- monochlorodibenzofuran (2-MCDF) detected as pollutants on teratogenicity and drug metabolic enzyme inducing potency were examined. Safety assessment of these chemicals was performed using the data obtained in these in vivo and in vitro experiments.

1. Effects of 2-MCDF on embryo-fetal development of rats were examined in an in vivo experiment, and compared with those in the in vitro teratogenicity test using the rat embryo culture system. 2MCDF (0, 250, 500, 1000 mg/kg/day) was given by gavage to pregnant rats during gestation days (GD) 9-11, corresponding to the culture period in the in vitro test, and embryo-fetal development was examined on GD 11.5 and 20. In the pregnant experiment, unlike in the in vitro test, no effects of 2-MCDF on embryo-fetal development were observed. As for the evaluation of the teratogenicity of 2-MCDF, however the present results agreed with the in vitro ones. In the in vitro experiment, DF, the putatively nonteratogenic parent chemical, caused embryo toxicity similar to those by 2-MCDF, and therefore, it was inferred that 2-MCDF caused no increase in the incidence of malformations in the present experiment. From these findings, the in vitro teratogenicity test using the rat embryo culture system was considered to be useful for the safety evaluation of environmental contaminants with putatively strong toxicity, if some proper criterion, such as reference chemicals, could be available.

In an in vivo experiment using mice, 2-MCDF was given by gavage to pregnant mice during GD 6-15, and its teratogenicity was examined. As a result, 2-MCDF caused hypertrophy of the maternal liver and an increased incidence of skeletal variation of the fetuses, but no teratogenicity was observed. The no observable effect level for fetuses was estimated to be 250 mg/kg/day, and for dams, less than 125 mg/kg/day.

2. 2-MCDF and 3-MCDF induced rat liver microsomal drug metabolizing activities dose dependently. The doses by which ethoxycoumarin deethylation were induced to two times of control were 167 mg/kg for 3-MCDF and 187 mg/kg

for 2-MCDF. These values were not so different from the values estimated by in vivo experiments, suggesting that in vitro test system using primary cultured rat hepatocytes can be applied to estimate the drug metabolism inducing activities in vivo for methylcholanthrene type of drug metabolism inducers.

From the present in vivo results and in vitro results reported in this study so far, it can be evaluated no risk of 2-MCDF detected at the concentrations (max 1.4 ng/l) in some tap water as a pollutant, in teratogenicity and inducing potency of drug metabolizing enzymes.

15. Estimation of Risk to Humans by Extrapolation from Low Dose

Animal Data: Toxicokinetic Studies

(FY 1988~1992)

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To generalize the biological significance of nitro reduction property for the toxicity of nitroarenes, three new 1-nitropyrenes substituted with a cyano group at 3-, 6-, or 8-position, that amplifies the electrochemical reduction of nitro group, were synthesized and their reduction property and mutagenicity were compared with those of 1-nitropyrene and dinitropyrenes. The half-wave potentials of the first and second electron reductions indicated that these cyanated 1-nitropyrenes were reduced easier than 1-nitropyrene for the electron-withdrawing effect of cyano substituent. These cyanated 1-nitropyrenes showed higher mutagenic activity in Salmonella typhimurium TA98 and TA98NR than 1-nitropyrene, and in particular, the mutagenic potencies in TA98 were almost similar to those of dinitropyrenes. These results indicated that the electrochemical ease of nitro reduction could be one of the fundamental factors responsible for the mutagenicity.

The plasmid carrying both acetyltransferase gene and nitroreductase gene was introduced into Salmonella typhimurium TA98 and TA100. The resulting strains, YG1041 and YG1042 showed high levels of both enzyme activities and were more sensitive to the mutagenic action of 2-nitrofluorene, 1-nitropyrene and p-nitrophenetole than the sensitive strains previously established. These results indicate that the new strains permit very

efficient detection of mutagenic nitroarenes in the environment.

1-Nitropyrene (1-NP) and its derivatives were assayed using rat embryonic cell differentiation systems. In the midbrain cell differentiation assay, the inhibitory activities of the compounds were in the following order: 1-nitropyrene-3,6-quinone > 1-nitrosoquinone > 1-nitropyrene-3,8-quinone > 1-nitro-6-hydroxypyrene > 1-nitro-8-hydroxypyrene > 1-NP > 1-aminopyrene > 1-acetamidopyrene > 1-nitro-3-hydroxypyrene. 1-Nitrosopyrene and 1-acetamidopyrene showed the stimulative effects on the differentiation of limb bud cells. The quinone and nitroso derivatives of 1-NP, therefore, showed greater teratogenic potential than 1-NP itself.

Five retinoids were tested by both rat whole embryo culture (WEC) and limb bud cell culture systems. The concentrations of the retinoids leading to effects on conceptus dysmorphogenesis in vitro and to 50 % inhibition of limb bud cell differentiation in vitro correlated very well with the lowest teratogenic doses in vivo. However, the limb bud cell culture system was found to be more sensitive than the WEC in detection of the activities of the retinoids.

The disposition of 1,6-dinitropyrene (DNP) in male F344 rats was investigated over 7 days. In 7 days after intraperitoneal administration of ^{14}C -1,6-dinitropyrene (1 $\mu\text{mole/kg}$), 64% of the dose was eliminated in faeces and 10% in urine. The rate of biliary excretion of radioactivity was 37% of the dose in 48 hr and the studies revealed involvement of enterohepatic circulation in the disposition of DNP. The elimination of DNP from plasma can be described by a two-compartment pharmacokinetic model and the elimination half-life was estimated from blood data to be 147 hr. High radioactivity was present in the adipose tissue at 7 days after an administration. The data from these studies suggest that DNP or its metabolites persist in the body for long periods.

The metabolism of urethane by mouse and human liver preparations using in vitro techniques was quantitatively compared. Isolated hepatocytes were prepared from adult male B6C3F1 mice and human liver specimens by collagenase perfusion methods and were incubated in modified Waymouth's 752/1 culture medium at 37°C. Incubations were conducted with urethane [^{14}C] at final concentrations of 0.01 and 1.0 mM, and samples were taken at 0, 1, 2 and 4 hr. Mouse hepatocytes in suspension culture converted 98 pmol/ 10^6 cells of urethane to CO_2 . DNA binding was detectable in mouse liver cells, and demonstrated dependency on incubation time and urethane concentration. DNA binding of 0.01 mM urethane increased linearly with time to 18 pmol/mg DNA by 4 hr. Protein binding of this concentration of urethane

was somewhat higher at 36 pmol/mg protein after 4 hr. Binding to protein at 1 mM urethane was 226 pmol/mg protein suggesting that it became saturated at the higher concentration. This effect was not observed in DNA binding which was 2400 pmol/mg DNA at 1 mM urethane. Covalent binding could not be determined in human hepatocytes because a high background interfered and the data obtained were variable.

16. Safety Assessment of Microorganisms Used for
Recombinant DNA Technology (FY 1989-1991)

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Biological, genetical and biochemical characterization of various strains of Bacillus thuringiensis and Pseudomonas spp. has been carried out which are expected as genetically engineered microbial pesticides or controllers of environmental pollution in future. The studies described below were done for the safety assessment of these bacteria used for the pesticides or the controllers.

1). Quantitative method for detection of small amount of lipopolysaccharide (= endotoxin) in Pseudomonas aeruginosa has been devised using 3-hydroxymyristic acid as a chemical marker. After conversion to methylester, the marker was coupled with anthracene-9-carboxyl chloride, a fluorescence probe. The resulting material showed maximum emission with excitation wavelength at 257 nm and emission wavelength at 458 nm in dichloromethane. Using the method, as little as 100pg endotoxin was easily detected in aqueous solution.

2). Rapid method for identification of Bacillus thuringiensis has been developed by using specific anti H (flagella) sera or DNA probes derived from insect toxin genes. With these methods, the occurrence of Bacillus thuringiensis has been investigated in various kinds of foods. As compared with the high incidence of Bacillus cereus, a food-poisoning bacterium, Bacillus thuringiensis were not detected at high frequencies in foods except for imported corns. Bacillus thuringiensis serovar kurstaki and aizawai used as microbial pesticides were found at high frequencies in the corns.

3) Both Bacillus thuringiensis kurstaki and aizawai contained various sizes of plasmids. Analysis of the plasmid profile was found to be useful for the epidemiology of these serovars; kurstaki was divided into six groups, and aizawai two groups on the plasmid profile.

4). Vegetative cells of Bacillus thuringiensis kurstaki and aizawai were found to be highly UV-sensitive. Spores of these strains were more resistant to UV ray than Escherichia coli K-12 WA921, but were inactivated completely by long term irradiation of UV. In the absence of UV ray, spores of Bacillus thuringiensis were highly stable and could not be inactivated at all in soil at 25°C for at least seven months. Bacillus thuringiensis could grow well on cabbage leaves at 25°C or 32°C for three to seven days in an incubator.

5). Diarrheal toxin similar to that in Bacillus cereus was detected at relatively high frequencies in various strains of Bacillus thuringiensis of food origin. The toxin was also produced by Bacillus thuringiensis serovars kurstaki and aizawai used for microbial pesticides. The amount of the toxin was higher in kurstaki than in aizawai. Like Bacillus cereus toxin, the toxin was unstable and was inactivated considerably during the purification procedure.

6). Type II restriction endonucleases were detected at a frequency of 10 % in Pseudomonas aeruginosa and of 2 % in Pseudomonas cepacia of different origin. One of the restriction endonucleases in Pseudomonas aeruginosa designated PaePs7I was shown to be an isoschizomer of XhoI whose recognition sequence is CTCGAG.

7). Large fragments (more than 100 bp) of repetitive sequences which appeared as inverted repeats could not be detected in Bacillus thuringiensis kurstaki using the method of Otsubo. IS sequences (IS1, IS600, IS629, IS630 and IS640) frequently detected in Escherichia coli and Shigella spp. were not detected in any strains of Bacillus thuringiensis kurstaki, Bacillus cereus F4433/77 or Pseudomonas aeruginosa Ps9.

17. Evaluation Methods for Biological Effects of Rare Earth
Metals

(FY 1989 - 1991)

National Institute of Hygienic Sciences

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Recently, rare earth metals attract our attentions as new promising materials in the pioneering technological industries as basic matters for superconductive substances, ceramics and amorphous substances. However, very few were reported on the biological effects of rare earth metals. The present studies were carried out to get basic data for safety evaluation of these metals.

Eu and Gd were administered orally to male and female rats at levels of 40, 200 and 1,000 mg/kg as their chlorides for 28 days. The remarkable decrease in body weight gain, accompanied with the decrease in food consumption, was observed in the male and female rats of both high dose groups. The female rats in the middle dose group of Eu also showed the decrease in body weight gain. The increase in adrenal weight and the decrease in thymus weight were observed in the male and female rats of high dose groups, respectively. The reduction of TP in serum was observed in the male and female rats of both high dose groups, as well as in high dose

groups of Y and La reported previously. This suggests that the metabolism of protein was affected with the administration of these metals. Changes in stomach and lung due to the irritation effect by rare earth metals were also observed. Both of Eu and Gd were accumulated in liver, kidney and bone, compared that La was accumulated in liver and Y was in kidney and bone. The Effect on Fe concentrations in liver, kidney, spleen and serum, and the reduction of Ba and Sr concentrations in bone was observed. Maximum non-effect levels were 40 mg/kg for the male and female rats of Y and La and for the female rats of Eu and Gd, and 200 mg/kg for the male rats of Eu and Gd, respectively.

The metabolism of Dy, Eu, Yb and Y, and the effects on the concentrations of Ca, Mg, Fe and P in the organs were investigated in the male rats by iv administration of their chlorides at 10 and 50 mg/kg as metals. These metals disappeared from blood within 1 day after administration, and were accumulated in liver, spleen and femur in high concentrations after 8 days. The higher the dose was, the more ratio of accumulation of dosed metals was found in spleen and the less in bone. The difference in distribution pattern among metals was observed. The half lives of dosed metals in blood and liver was calculated as 0.37-6.06 hours and 12.9-18.0 days, respectively. Ca concentrations in liver and spleen, where dosed metals were accumulated, were found to be high.

The distribution of Y, La, Ce, Sm, Nd, Eu, Tb, Gd, Dy, Ho, Er and Yb in liver, kidney, spleen, pancreas, lung, heart, seminal vesicle, testis, muscle, bone, thymus, submaxillary gland and brain were examined in the male mouse by iv administration of their chlorides at 25 mg/kg as metals. After 20 hr, these metals were accumulated in high concentrations in spleen, lung and liver, where Ca concentration also increased remarkably. Good correlation ($r = 0.905$) was found between concentrations of dosed metals and Ca in spleen. However, concentrations of Mg, Fe, Zn and P in the organs were not affected with the administration of these metals.

⁴⁵Ca and ³²P were administered orally to the male rats pretreated with Tb orally for 4 weeks (100 mg/day/animal as metals), and excretion of them to urine and feces was measured daily for 10 days. The amount of ⁴⁵Ca and ³²P excreted to feces increased remarkably in Tb-pretreated rats compared to control rats (15 → 45% and 8 → 65%, respectively), whereas those excreted to urines reduced by Tb-pretreatment (1 → 0.2% and 12 → 2%, respectively). Tb-pretreatment showed the same inhibitory effect on the

absorption of Ca and P from rat intestine as La-pretreatment reported previously. The mechanism of inhibitory effect of rare earth metals on the Ca absorption from intestine was investigated in vitro using the mucous membrane fraction of rat duodenum, and Ca binding capacity of the fraction was found to be completely inhibited in the presence of high concentration of Tb.

The intestinal absorption of L-histidine were examined in situ using mouse intestine after pretreatment with La, Tb, Y, Be, V and Mo. The results showed that intestinal absorption of L-histidine was inhibited at levels of 0.5-2 mM of V, 2-4 mM of La and 4 mM of Tb and Be. However, Y and Mo showed no inhibition up to 4 mM.

18. Effect of Organochlorine Compounds on the Lung Immunity
to Respiratory Pathogens
(FY 1990~1992)

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I. *In Vitro* Cellular Model II for Respiratory Infection

In order to estimate the effect of organochlorine compounds on infection and immunity of respiratory pathogens, we developed an *in vitro* cellular model for infection with *Legionella pneumophila* and *Mycoplasma pneumoniae* using mouse peritoneal macrophages and human peripheral blood mononuclear cells (PBMC) respectively.

The lung macrophages and thioglycolate (TGC)-elicited peritoneal macrophages from A/J and MPS mice, but not in those from B10.A mice were permissive for *Legionella* growth. The resident peritoneal macrophages from all strains of mice tested here were nonpermissive. Because the number of lung macrophages recovered from mice was very small, we used TGC-macrophages rather than lung macrophages for *legionella* infection *in vitro*. After interferon (IFN)- γ or lipopolysaccharide (LPS) pretreatment, even the permissive macrophages from A/J and MPS mice became resistant to infection (Induced resistance). We found that both natural and induced resistance of the macrophages to *legionella* infection attributed to a L-arginine independent mechanism. Using the *in vitro* model, we estimated the effect of organochlorine microbicides, chlorothalonil (TPN) and captan (CAP); and organochlorine solvents, trichloroethylene (EC13), tetrachloroethylene (EC14), and carbon tetrachloride (CCl4) and found that the degree of the organochlorine effects on the phagocytosis and the bacterial growth in macrophage cultures were different among the strains of mice (Fig.1).

The cell lysates of *Mycoplasma* induced the blastogenesis of human PBMC and stimulated the PBMC to produce various kinds of cytokines. In the cytokine assays, we found that tumor necrosis factor (TNF) production was inhibited by TPN pretreatment (Table 1) and that the organochlorine sol-

vents did not affect the TNF production so much.

These results showed that organochlorine pollutants suppress the antibacterial activity of macrophages against respiratory pathogens and may suggest that the pollutants make the human being more susceptible to respiratory infection.

Fig.1 Effect of organochlorine compounds on the growth of *Legionella* in the macrophage cultures from B10.A and C3H/He mice (24-hr pretreatment followed by 4-d coculture; numbers in columns: concentrations (ppm))

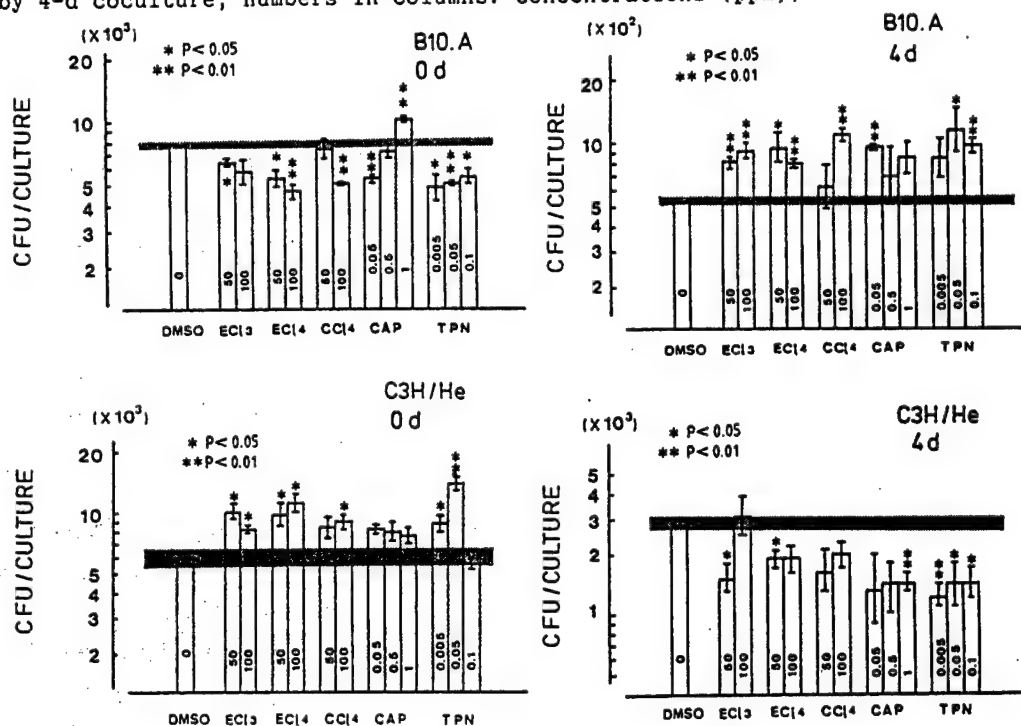


Table 1 Effect of TPN on the TNF production by human PBMC stimulated with PHA and Mycoplasma cell lysate

| TPN (ppm) | TNF (Units /ml) from PBMC stimulated with : | | |
|-----------|---|----------|----------------------|
| | None | PHA | <i>M. pneumoniae</i> |
| 0.000 | < 2.0 | 53.2±9.8 | 12.3±2.6 |
| 0.007 | < 2.0 | 18.1±1.5 | 18.8±2.1 |
| 0.030 | < 2.0 | 2.5±1.3 | < 2.0 |
| 0.125 | < 2.0 | 8.4±4.3 | < 2.0 |
| 0.500 | < 2.0 | 8.6±5.7 | < 2.0 |

19. Studies on the Influences of Chemical Control on the Target and Non-target Populations with Special Reference to Insecticide Resistant Mechanisms
(FY 1990 ~ 1992)

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Researches of following items were carried out in 1991.

1. Insecticide resistance of the housefly at the landfill disposal site of the Bay to Tokyo.
 2. Resistance to an IGR, diflubenzuron, developed in a field population of the housefly.
 3. Insecticide susceptibility of a non-target insect species, *Drosophila melanogaster*.
 4. Role of carboxylesterases in organophosphate of *Culex molestus*.
 5. Influence of a pyrethroid insecticide on the metabolism in the housefly.
-
1. The resistance to organophosphorus insecticides in the housefly of Tokyo bay dumping site in 1991 remained a high level as in last several years but the mixture of propetamphos and dichlorvos was showed to be effective. The resistance to pyrethroids and IGR (diflubenzuron, pyriproxyfen) was at low level. However, the frequency of kdr gene, a major factor of pyrethroid resistance, was found to be over 0.10 for the first time at the investigation in November. This value supposes that the possibility of spread of kdr gene throughout the population by the future frequent and large-scaled use of pyrethroid insecticide in the area.
 2. In the horticultural area in Shizuoka and Shimizu cities, resistant house flies to a chitin synthesis inhibitor, diflubenzuron, outbroke in 1991 due to the several years control using the insecticide against the housefly which reproduced in manure put in the soil. The population of the housefly showed cross resistance to a JH mimic, pyriproxyfen, which had not been used in the district. Another IGR, cyromazine, had a high activity to the housefly population.
 3. Levels of insecticide susceptibility of *Drosophila melanogaster*, a non-target species, varied with their habituating locations which had specific histories of the chemical control. Colony in Tokyo bay dumping site showed very high resistant level against DDT, and colonies of all locations tested were found to reduce the

susceptibility to permethrin and fenvalerate. Considering that susceptible strain of the fruit fly, Oregon-R, also showed a certain level of pyrethroid tolerance comparing with the housefly, the species of *Drosophila melanogaster* itself seems to have some resistant factors against pyrethroids.

4. A resistant strain (Shinjuku) of *Culex pipiens molestus* against organophosphorus insecticides has 25 times more amount of B-type carboxylesterase comparing with a susceptible strain Totsuka. Measurement of carboxylesterase and acetylcholinesterase inhibition in the resistant larvae treated with organophosphates indicated the sequestering role of carboxylesterase in the resistance. Another carboxylesterase found in intestine of the larvae which had very high affinity to organophosphates was also shown to have the role.

5. In the housefly, sublethal dose of permethrin elicited abnormality of sugar metabolism. NMR analysis showed that sugars were metabolized through anaerobic pathway at the time of paralysis by permethrin treatment, and especially glycerol decomposition was disturbed.

20. Study on Distribution of Metals in Soils in Japan for Evaluation of Environmental Pollution and of Health Effects by Their Utilization in Advanced Industry with Technical Progress

(FY1990-1994)

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Investigation of the distribution of metal elements, of which amounts of utilization in advanced industry with the technical progress are increasing, in soils in Japan is very important to evaluate their environmental pollution and health effects.

Based on the preliminary experimental conditions examined in sampling, sample preparation and ICP emission spectroscopy in the first year, in this year the concentration of the heavy metals in soils at some spots of Hokkaido and Tohoku areas in Japan was measured. In addition, the improved analytical method of gallium (Ga) by graphite furnace AAS was investigated. In order to make sure the vital influences and safety evaluation of elements in the boron group, acute influence for the small experimental animals by oral administration of the compounds and the effect of administered compounds on metabolism of heme and porphyrin in rat organs and human blood were examined. The results obtained are as follows.

1. The study of the application of developed methods to the analysis of trace metals and Ga related the high technology industry in the soil.

i) The sample preparation by the acid decomposition with HNO_3 - HCl - HClO_4 - HF and the geological and regional sum up of analytical data by multitype ICP.

① From the results of geological analysis, the concentration and composition ratio of Al, Pb, Mn, Ti and P in soil are in fair agreement with the that of the rock in the same place. However, the composition ratio of Ca, Mg, Na and K varies.

② From the results of regional analysis, it seems that five elements such as Al might be useful to speculate the average background values in the soil because of the good agreements with the data between three prefectures. But, in the case of four elements such as Ca, it is necessary to determine the background values depending on the regional area because of variation among the prefectures.

ii) The determination of Ga by graphite furnace atomic absorption spectrometry with matrix modifier.

With the aid of the treatment of carbon tube cuvette with tantalum and the addition of EDTA as matrix modifier, the positive interference by Al, Mg, etc. and negative interference by chloride ions were reduced. It was suggested that it might be possible to determine the trace gallium in biological materials like calcium phosphate as principal constituents.

2. Some experimental investigations on rats, mice and human blood for evaluation of health effects by metal elements in the boron group were carried out as follows.

i) Acute toxicity in rats after oral administration of some metal compounds in the boron group.

① Each ratio in getting their body weight on 7th day after oral administration of GaAs, Na_2HAsO_4 , or $\text{Ga}(\text{NO}_3)_3$, was suppressed.

② In rats on 7th day after the administration of GaAs, a significant increase in relative ratio of some organs' wet weight against their body weight was dependent on the significant decrease in their body weight.

③ Marked increase in content of lipid-peroxide in organs of rats after the administration of GaAs, Na_2HAsO_4 , or $\text{Ga}(\text{NO}_3)_3$, was observed on 7th day. In the liver, particularly, there was a relationship between the increase in content of lipid-peroxide and the decrease in contents of water-soluble reductive substances like total thiol and vitamin C.

ii) Change of tellurium (Tl) content in organs and excrement of mice after oral administration of Tl acetate.

① Most high content of Tl was detected in kidney of mice.

② Content of Tl in organs of mice was decreasing day after day. The content on 7th day about 10% of that on 1st day. Main part of decreased Tl was excreted into feces.

iii) Effects on metabolism of heme and porphyrin *in vitro* experiments.

① Activity of ALA-D in the peripheral blood was depressed by $\text{Ga}(\text{NO}_3)_3$, InCl_3 and $\text{Tl}(\text{NO}_3)_3$ in low concentration. Activity of purified ALA-D of liver from rabbits was, also inhibited by nitrate compounds of Ga and Tl. Style of their inhibition was non-competitive one.

② Inhibition of ALA-D by GaAs seemed to be caused by Ga, because arsenide compounds did not inhibit it. This inhibition could not be recovered by addition of activators like DDT or Zn^{++} . The inhibition of ALA-D activity in mixture with GaAs was increased during pre-incubation or freezing for long time.

③ Purified PBG-D from bone marrow of rabbits and PBG-D in human peripheral blood were significantly inhibited.

iv) Effects on metabolism of heme and porphyrin *in vivo* experiments.

① Coproporphyrin content in erythrocytes of rats on 1st day after oral administration of GaAs, $\text{Ga}(\text{NO}_3)_3$, of Na_2HAsO_4 , increased up to 5.9, 3.2 or 2.1 -fold, respectively, in comparison to that of control group. However, Zn-protoporphyrin content after the administration of $\text{Ga}(\text{NO}_3)_3$ and free protoporphyrin content after the administration of InCl_3 were shown 40% and 69%, respectively.

② InCl_3 , $\text{Al}(\text{SO}_4)_3$ and TlNO_3 inhibited the activity of PBG-D in bone marrow, but did not in liver.

From these results *in vivo* experiments, it seems that metal compounds in the boron group might have marked influence on the metabolism of heme in erythropoietic tissues and kidney.

21. Studies on genetic damage and its' biological effects by organochlorine environmental pollutants and on their modification by nutritional conditions
(FY 1991-1993)

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Damaging effect of various organochlorine chemicals on DNA was determined by in vivo sister-chromatid exchange (SCE) analysis of bone-marrow cells and an analysis of 8-hydroxy-deoxyguanosine (8-OHdG) being an index of oxidative damage of hepatic DNA.

The chemicals were daily administered to mice at one-fifth of lethal dose for 5 days. Among the examined chemicals, significant increase in SCE with heptachlorepoxyde, trichloroethylene and 3-chloro-2,4-dibromopropane were observed. However, their inductions were weak compared with that by cycloheximide using as positive control.

Although the contents of 8-OHdG in the hepatic DNA were determined in mice administered sixteen organochlorine chemicals, no chemical tested did significantly increase in 8-OHdG.

Last year, trichloroethylene (TCE) was reported to have a weak effect on DNA single strand breaks. Moreover, TCE was detected slightly to induce SCE in bone-marrow cells. Considering the high dose of TCE in both experiments, the effect of TCE on DNA damage seemed to be weak.

In the next experiment, the difference in DNA damage by TCE was determined by using three strains of mice. TCE was lethal and easily induced SCE in bone-marrow cells in C3H strain, but not in ICR and B6C3F1 mice.

22. Effect of Environmental Substances on Defense
Function in Immuno-deficient Patients
(FY 1991 - 1993)

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1. Effects of trichloroethylene and tetrachloroethylene on neutrophil function and IL-8 production of mononuclear cells in immuno-deficient patients.

Trichloroethylene and tetrachloroethylene did not affect on O₂⁻ production, release of myeloperoxidase, beta-glucuronidase and chemotaxis for IL-8 in neutrophils of adult healthy control. However, production of IL-8 from mononuclear cells in adult healthy control was inhibited with trichloroethylene and tetrachloroethylene. In patients with immuno-deficiency such as juvenile rheumatoid arthritis, systemic lupus erythematosus, glomerulonephritis, neutropenia, and Felty, these functions were resulted as follows (Table 1).

1. O₂⁻ production: In juvenile rheumatoid arthritis, tetrachloroethylene slightly inhibited the activity. However, trichloroethylene strongly inhibited it in a dose-dependent fashion. In neutropenia, tetrachloroethylene at a low concentration inhibited it, but activated it at its higher concentration. In glomerulonephritis, trichloroethylene inhibited it, but tetrachloroethylene activated it at concentration of 30 ppm.
2. Myeloperoxidase release: In juvenile rheumatoid arthritis, tetrachloroethylene slightly inhibited the activity. trichloroethylene strongly inhibited it. In systemic lupus erythematosus, glomerulonephritis, neutropenia, Felty, both substances did not affect it.
3. beta-glucuronidase release: In juvenile rheumatoid arthritis and systemic lupus erythematosus, tetrachloroethylene did not affect the activity. However, trichloroethylene inhibited it in a dose-dependent fashion. In glomerulonephritis, both substances did not affect it.

4. Chemotaxis for IL-8: In most of neutrophils in patient tested, the activity was inhibited with both substances.
5. IL-8 production from mononuclear cells: Production of IL-8 from mononuclear cells in patients was slightly inhibited with tetrachloroethylene or trichloroethylene as well as in adult healthy control.

Table 1. Effect of tetrachloroethylene or trichloroethylene on Neutrophil Functions.

| | O ₂ ⁻ | | MPO | | BGL | |
|-------|-----------------------------|-----|-----|----|-----|-----|
| | TE | TR | TE | TR | TE | TR |
| JRA | - | + | + | ++ | +/- | + |
| SLE | (-) | (-) | - | - | - | ++ |
| GN | - | * | - | - | + | + |
| NP | - | - | - | - | - | - |
| Felty | (-) | (-) | - | - | (-) | (-) |

JRA: juvenile rheumatoid arthritis

SLE: systemic lupus erythematosus

GN: glomerulonephritis

NP: neutropenia.

MPO: myeloperoxidase, BGL: beta-glucuronidase.

TE: tetrachloroethylene, TR: trichloroethylene

++: inhibition, +: slight inhibition, *: increase, -: no effect

23. Development of a Convenient In Vitro Assay to Screen for Substances that Initiate or Enhance the Allergic Reaction to Japanese Cedar Pollen (FY 1991-1993)

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The number of allergic patients, especially those with allergies to Japanese cedar pollen, has recently increased dramatically. From an etiologic point of view, there appears to be a causal relationship between air pollution and the prevalence of disease. We have developed in part an in vitro experimental system to analyze substances that enhance the IgE antibody to Japanese cedar pollen, since it has been shown that the IgE antibody is highly associated with the induction and/or aggravation of allergic diseases.

First, an allergen was extracted from Japanese cedar pollen. Two liters of NaHCO_3 (0.15M, pH 8.0) was added to 100 g of pollen and the mixture was incubated for 30 min on ice. The pollen was separated from the supernatant by centrifugation, and hexadecyltrimethylammonium bromide (Sigma) was added to the pollen to a final concentration of 0.1 %. After incubation for 60 min on ice, the protein fraction was precipitated by 80 % saturated $(\text{NH}_4)_2\text{SO}_4$ and collected by centrifugation. The pellet was resuspended in Tris-buffered saline (pH 7.8), dialyzed against the same buffer, and treated with DEAE cellulose in a batch method. The treated fraction was dialyzed against 0.01 M acetate buffer (pH 5.0) and applied to a CM cellulose column. Elution was carried out in a stepwise fashion, first using acetate buffer and then 0.1 M phosphate buffer containing 0.3 M NaCl. The second fraction was subjected to electrophoresis. Two bands were obtained around 40 KDa, and called sugi basic protein (SBP). These bands were confirmed to be reactive with anti-SBP antibody by Western blotting.

BALB/C mice were immunized with 10 ug SBP in alum, challenged two weeks later, and finally boosted 3 days before fusion. The SBP-primed spleen cells were fused with SP2/0 myeloma cells and hybridomas were selected using HAT (hypoxanthine/aminopterin/thymidine) medium by a standard method. The hybridomas reactive with SBP antigen were screened by cell enzyme-linked immunoassay. Four kinds of SBP-reactive hybridomas were obtained, all of which were positive in terms of class II molecule expression. When spleen cells or lymph node cells primed with SBP antigen in vivo were cultured with the same antigen in vitro, proliferating cells were observed. These cells were stimulated with an antigen and Con A-stimulated rat spleen cell culture supernatant, alternatively. After limiting dilution using antigen

presenting cells and antigen, three kinds of T cell clones reactive with SBP were established. These cells expressed CD3 and CD4 and proliferated by stimulation with antigen and antigen presenting cells.

We purified a major allergen called SBP from pollen and established several SBP-specific B cell hybridomas and T cell clones. Furthermore, macrophage hybridomas with the capacity to present an antigen to T cells were also obtained. These kinds of cell lines will be valuable for analyzing SBP-specific IgE antibody production and IL4 production at the clonal level, and will be useful for evaluating allergy-enhancing substances.

24. Problems caused by nitrogenous pollutants in domestic water use and their control
(FY 1991 - 1995)

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Keisuke Fujiwara and Masahiro Fujiwara
Research Committee

This study was newly started for the purpose of elucidating the problems caused by nitrogenous pollutants such as ammonia and nitrate in water and developing appropriate ways to control their concentrations. Some water purification plants taking surface water suffer from high ammonia concentration in raw water because it is difficult to maintain residual chlorine concentration after prechlorination at a desirable level. In such a case, other problems related to prechlorination, e.g. formation of hazardous chlorination by-products, also occur. Nevertheless, no effective measures are taken for control of ammonia in surface waters. On the other hand, a high nitrate/nitrite nitrogen concentration of more than the drinking water quality standard is found in some groundwaters used for water supply.

The objectives of this study are:

- 1) To elaborate a rational control level of ammonia nitrogen concentration in public water bodies through investigation on the problems in water purification caused by ammonia,
- 2) To identify the causes and significance of groundwater contamination by nitrate, and
- 3) To develop a new efficient removal method of nitrate in ground-water.

We laid emphasis on review of scientific papers and past data on this topic in the first year of five-years' research period. Basic information on the followings was collected:

- 1) Health effect of nitrogenous compounds in drinking water,
- 2) The problems in surface water purification caused by ammonia,
- 3) Current control systems of prechlorination process,
- 4) Occurrence of halo-acetonitriles in purified waters,

5) Groundwater contamination by nitrate, and

6) Current technologies for nitrate removal from groundwater.

In addition, a series of laboratory experiment started for development of a new efficient removal method of nitrate in groundwater applying biological denitrification-membrane filtration.

The main findings of the study in this fiscal year are as follows:

- 1) Although river and ground water contamination by nitrogenous compounds is a significant problem from a couple of decades ago, it has not been improved so much yet. Groundwater contamination by nitrate seemed to become more serious than before.
- 2) The higher is the ammonia concentration in river water or the more its fluctuation, the more difficult is proper prechlorination in a water purification plant taking the water as raw water.
- 3) It has been found that halo-acetonitriles are formed by chlorination of water. However, their precursors and the mechanism of their formation are not yet clear.
- 4) It is well known that nitrate in drinking water causes methaemoglobinemia. Further information should be collected about the relationship between stomach cancer and N-nitroso compounds formed from nitrate in a stomach, and the health effect of nitrogenous compounds including halogenated nitrogenous organic compounds.
- 5) The result of a preliminary experiment on nitrate removal by biological denitrification-membrane filtration using hydrogen gas exhibited a denitrification ratio of approx. 80 percent under the condition of nitrate nitrogen load of $1\text{kg/m}^3/\text{day}$.

Based on these findings, it is planned to continue the study on ammonia behavior in a water purification plant and improvement of prechlorination control system in the next fiscal year. Regarding nitrate in groundwater, the main points of next-year's study will be survey on small-scale drinking water sources, the interrelationship between groundwater contamination and land use characteristics, and effects of the environmental conditions and other factors on nitrate removal in biological denitrification-membrane filtration process.

25. Technical Development for Ecological Control of Noxious Red Tides
(FY 1989~1993)

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The objective of this study is to develop a technique to control noxious red tides ecologically by taking advantage of growth-antagonistic relationship between diatoms and harmful flagellates without using any chemicals. The project is composed of elucidation of, 1. ecological features and formation mechanisms of resting cells in diatoms, 2. succession mechanisms of phytoplankton, and 3. nutrient dynamics and technical aspects for ecological control.

The third year's results are summarized as follows:

1. Resting cells of the centric diatom *Skeletonema costatum* were produced in culture. The conditions of low light intensities (or darkness) were essential for the resting cell formation.

2. Total number of the diatom resting cells of *Skeletonema costatum*, *Chaetoceros* spp. and *Thalassiosira* spp. in bottom sediments of Harima-Nada were $2.09 \times 10^2 - 2.89 \times 10^3$ /cm wet sediment (mean, 1.14×10^3) in May, and $1.03 \times 10^2 - 3.23 \times 10^3$ /cm wet sediment (mean, 6.54×10^2) in July, 1990. In northern Hiroshima Bay, the densities of diatom vegetative cells fluctuated drastically in water columns, but that of resting cells did not so in sediments.

3. Effects of light intensity on the germination (or rejuvenation) of diatom resting cells were examined using sediments of northern Hiroshima Bay. In general, diatom resting cells needed light ($> 5.8 \mu\text{E}/\text{m}^2/\text{sec}$) for germination (or rejuvenation).

4. The cysts of the red tide flagellate *Heterosigma akashiwo* could germinate at 10°C , and showed vigorous germination at 15°C or higher temperature. The cysts of *H. akashiwo* did not need light for germination.

5. Effects of abiotic factors such as light intensity, water temperature and salinity on growth of diatoms were examined and the growth param-

ters for each diatom were identified. Available amino acids for harmful flagellate, *Gymnodinium nagasakiense* and diatoms were elucidated under axenic culture experiments.

6. During early June to early September in 1991, dominating phytoplankton in southern Harima-Nada was diatoms and harmful organisms was not observed at high cell density. The dominant diatoms were *Leptocylindrus danicus*, and *Nitzschia* spp. in June, *Chaetoceros* spp. in July, and *Skeletonema costatum* in August. Relationships between annual changes of precipitation (or specific gravity) and diatoms abundance in southern Harima-Nada over 7-years (1985-1991) were analyzed statistically. As the results, no significant correlation coefficient between these was detected. However, the correlation coefficient between silicate concentration and diatom abundance alone was fairly significant.

7. Kinetics on the growth of four kinds of diatom were investigated by means of axenic culture of diatoms under the limitations of phosphorous and nitrogen concentrations and several growth parameters were identified. Also, application of these parameters to an embayment were examined.

8. Polysaccharide-protein complex extracted from *Chaetoceros* cells inhibited the cell division of axenic *Chattonella antiqua*. The protein component was fractionated from the complex by means of DEAE-ion exchange chromatography and the main components were found to be aspartic acid, glycine and leucine. Macromolecular dissolved organic substances collected from seawater samples of Harima-Nada also inhibited the growth of *Skeletonema costatum* but not the growth of *C. antiqua*.

9. Nutrient liberation from bottom sediments was examined by using the samples collected from Harima-Nada in summer. It became clear that various nutrients were released actively from the samples under different conditions, namely under aerobic condition for nitrate-N, under oxygen-deficient condition for ammonia-N and phosphorus-P, and under both conditions for silicate-Si. It was suggested that existence of many benthos in sediments had some influence on nutrient liberation from the sediments.

10. The diatom resting cells survived longer (at least 3 years) under lower storage temperature (11°C or below) than higher storage temperature.

11. The cysts of *H. akashiwo* could also survive for long time under lower storage temperature (11°C or below).

12. Annual change in cell density of *Gymnodinium nagasakiense*, showed bimodal cycle according to interaction of replacement rate of the seawater and growth rate of the organisms. On the other hand, cell density of diatoms had several peaks through the year and the multiplication of diatoms closely related to supply of nutrient salts, particularly silicate from rivers.

26. Study on the Optimal Allocation Method

of Green Resources by the Synthetic Assessment

(FY 1991-1993)

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As urbanization and industrialization in Kansai area, the social needs for non-timber-uses of forests have been increasing. Wildlife, landscape, recreation and environmental conservation are included in non-timber uses. There is no established planning procedure to utilize forest to meet such a variety of needs for forests as "green resources". Now Kansai has come to recognize the importance of green resource, and the proper planning procedure to optimize the allocation of green resources is now urgently required by all levels of the governments. This research program intends to develop the procedure of the allocation of green resources by the synthetic assessment.

1. Development of the procedure to assess social demands and environment

To assess the social needs for green resources, views and opinions of the landowner themselves on green resources were investigated at first by interviews. Also, to estimate the social demands for green resources in Kansai the number of the visitors in green resources area was estimated by fuzzy programming method. Investigations to develop assessment procedures,

which can facilitate as geographical information system, based on natural environment, such as soil types, topography, vegetations, soil conservation capacity, and water conservation capacity, have been started. For the development of assessment procedure based on both natural and social environmental informations of Hyogo Prefecture in Kansai area, a database describing them should be assembled in the format works on a microcomputer. More than 83 items have already been described in this database, and offered. This database will be used for the computerized spatial planning. Spatial planning will be carried out on the basis of zoning and typing of green resources, and zoning (urban, rural, high-mountains) or typing (timber, environment, conservation) methods based on social demands were investigated. In Kansai area soil and water conservation activities of forests were given the highest priority, and then wildlife, landscape, timber production in order.

2. Development of green resources planning procedure

For the computerized spatial planning method, various mathematical programming methods were compared, and the method of global criterion and the goal-programming method are clarified to be most suitable to the objective of this program.

To provide a pilot green resources plan for Hyogo Prefecture using the procedures developed on this project, preliminary research was conducted according to the policies of forest and land-use in Hyogo Prefecture at present time. No conflicting problems between these policies and our planning procedure were found.

27. A New Methodology Using Marine Fish to Evaluate
Toxic Effects of Pollutants on Marine Organisms
(FY 1987 - 1991)

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In freshwater a standard method was published in 1960 with the carp as a recommended test animal. However, no marine fish is accepted as a test animal in seawater toxicity tests. We are aiming at setting up a new method for toxicity tests in seawater. We have fulfilled Subtheme 1 Search and evaluation of a pollution-indicator marine fish in 1989, and Subtheme 2 Establishment of a standard feeding method in 1990.

3. Accumulation of pollutants and their metabolic pathways

Red sea breams were exposed in seawater containing various amounts of organotins for 8 weeks and depurated for 4 weeks. Calculated BCF did not fit with the usual BCF-Pow relationship, because of the fast uptake and the slow excretion of organotins.

Carp, red sea bream and mummichog were exposed to Cd in freshwater, 100% seawater(SW) and =0 to 100% SW respectively. The accumulation of

Cd in mummichog decreased suddenly in the liver, kidney and gills with increasing salinity from =0 to 25% SW, and more than 25% the Cd content did not changed. In the only intestine the Cd content increased with increasing salinity from =0 to 100% SW.

After the exposure to TBTO and Cu for 8 weeks, we histologically inspected various organs of red sea breams. Observed changes with TBTO were hypertrophy and necrosis of the hepatic cells, thickning and hyperplasia of respiratory epithelium of the gill, and with Cu were hypertrophy of the hepatic cells and atrophy of thymus. After 8 weeks of the exposure to Cu, we determined GOT, Mg, cholesterol, phospholipid, inorganic P, etc. in serum. GOT etc. increased and only glucose decreased in 4 weeks later, however, after 8 weeks there was no difference between the Cu exposed and control.

4. Establishment of Effect Evaluation Method and Making a Manual

Water flux in gills determined with THO is affected by the surface active agents. By the permeability change we can evaluate the effects of surfactants on fish.

We can usually observe a significant change of leukocytes one week after the exposure, and the change of erythrocytes (e.g. anemia) several weeks later. The critical organs (e.g. liver) affected by pollutants can be inferred by the change in serum components (e.g. GOT).

We recommend as histologically important organs; first the liver, kidney and gills, secondly the spleen, stomach and thymus, lastly the skin eye balls.

We must evaluate the BCF carefully, because the BCFs differ greatly (=10 folds) with experimental conditions. We have discussed comprehensively the acute toxicity test with red sea breams, Japanese anchovy and flatfish, and the bioaccumulation test with red sea breams in a static (8 days), a semi-static (4 weeks) and a flow system (8 weeks). We have published a MANUAL and distributed in March 1992.

28. Development of Nitrate Removal Techniques in the Shallow
Groundwater by using Agricultural Ecosystems
(FY 1991-1995)

| | |
|---|--------------|
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1) Transport of polluted groundwater through subsurface layers.

(1) Flow and diffusion mechanism in heterogeneous porous media.

In the first year, a new ground probing radar system which employed 2 GHz antenna, was completed to develop the surveying techniques for the evaluation of subsurface heterogeneous structure. The resolution of this system was experimentally proved to be high enough to detect and image clay layers of more than 5cm in thickness, existing 40 cm from the surface. For modelling the infiltration phenomena under unsaturated conditions, experimental studies were carried out using the sloping beds made of fine quartz sand and glass beads. It was possible to generate the fingering phenomena, a typical funneled flow in unsaturated zone. Occuring and growing process of fingers were recorded in an 8 mm video tape. This result was the first observation in sloping beds, and was very significant to clarify the behavior of pollutants in sloping beds consisted of several layers which had different physical characteristics each other. For research work on the groundwater flow under saturated conditions, an apparatus with three big sample cylinders, 180 mm in diameter and 500 mm in length, was prepared for permeability and tracer tests. A preliminary test was carried out using the standard sand. The soil blocks were sampled from three different layers, i.e., Kanto loam (volcanic ash soil), Kanuma tuchi (pumice), and an unnamed volcanic ash clay lied beneath Kanuma tuchi, at the test field in Kasama City. The heterogeneity of each soil structure was evaluated in soil analysis and X-ray CT imaging test. A fundamental technique with precise observation was developed to visualize the boundary layers growing with flow on the surface of discontinuity in porous media. A microscope was employed to observe the tracer movement and

evaluate the velocity distribution in a narrow pass of media. It was found that the boundary layer was thicker than theoretical one, and the velocity at the vicinity outside of the boundary layer was higher than the theoretically calculated values. Displacement thickness of the boundary layer was measured in the test carried out under the existence of films. These experiments were expected to clarify the influence of the boundary layers upon the flow and diffusion in heterogeneous media.

2) Evaluation and development of utilization technology of nitrate removal function from nitrate polluted groundwater in agricultural area.

(1) Analysis and evaluation of nitrate removal function of plained forest in an agricultural area.

In the plained forest studied (average age, 30 year; tree height, 13 m), the concentrations of ammonium (NH_4) and sulfate (SO_4) were higher in the upper soil layers, whereas electric conductivity (EC), and concentrations of nitrate (NO_3), sodium (Na), and chloride (Cl) were highest at the 200 cm depth. The nitrogen mineralization was observed only in the soil surface in an incubation experiment, though the initial amount of inorganic nitrogen was higher in the lower soil layers. The number of microorganisms related to the nitrogen metabolism was largest in the soil surface layer, followed by 150 cm depth, and relatively small on the 50 cm and 100 cm depth. This suggests that the denitrification would take place at the 150 cm depth, as well as in the soil surface layer. The parent material of the soil in this study area is a weathered volcanic ash, which consists of upper new Kanto loam, lower new Kanto loam, and dark brown crack layers. The Joso clay bed (aquiclude) underlies the ash layer,

and both the lower new Kanto loam and the dark brown crack layers form the aquifer of unconfined groundwater. The concentrations of NO_3^- , Na^+ , Cl^- , and SO_4^{2-} were relatively higher in the upland field and in the plained forest located near the upland field. This indicates that the water quality of groundwater is dependent on the field utilization above.

(2) Evaluation of nitrate removal function in agricultural area.

In the study site located in a sandy soil area in Kujukuri District, in Chiba Prefecture, the hydraulic gradient and variation in water table of groundwater accompanied with rainfall were observed by using 13 piezometers set in grids in the study area. The hydraulic conductivity determined by a pumping test was $2 \times 10^{-2} - 4 \times 10^{-2} \text{ cm sec}^{-1}$. The water movement in the study site was checked by a trace experiment using Cl as a tracer.

In an upland-paddy field area, the concentrations of inorganic ions such as Cl^- , SO_4^{2-} , and NO_3^- showed no difference with depth within each well, which is located in the upland field near paddy field, and at 50 and 450 m from the upland field margin in the paddy field respectively. The Cl^- concentration was not different among the wells, but the NO_3^- concentration was extremely low in the well located at 450 m from the margin. The nitrate removal rate of paddy field, which received groundwater containing NO_3^- in high concentration, was estimated as 5.3 kg N /ha/day during 55 days in July and August.

An acetylene inhibition technique was used to estimate the denitrification rates in submerged agricultural area. In the measurement of nitrous oxide by using an ECD gas chromatograph, a divergent flow path was set in the equipment in order to prevent acetylene reaching to the detector. Some measurements were made in a

reed wet land and in an irrigated pond.

(3) Development of utilization technology of nitrate removal function of agricultural area

Four paddy miniatures consisting of containers, irrigation pumps and tanks, and measuring apparatus were constructed to conduct fundamental experiments for improving the NO_3 removal efficiency in paddy field. The saturated hydraulic conductivity was measured in a gray lowland soil treated with various soil conditioners. Addition of rice straw (20% in weight), rice straw (5%) + charcoal (5%), or rice straw (5%) + super-water absorbent polymer (0.3%) increased the saturated hydraulic conductivity.

Fundamental survey was undertaken in an irrigation pond and a fallow paddy field. The inflow of groundwater containing higher concentrations of NO_3 was confirmed in the both study sites. A decline in nitrate concentration was noticed along the linked pond series.

29. Studies of Simulation Models of Suspended Particulates
Concentration from Industrial Emissions
(FY 1987~1991)

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Environmental pollution of suspended particulates (SPs) in Japan is still over the environmental standards, and urgent improvement is governmental concern. To satisfy these requirements, reliable simulation models which can figure out the contribution of industrial emission sources to environmental concentration is necessary.

This study has been performed to construct a physical simulation model of SPs concentration applicable to industrial areas. The following researches in both field and the laboratory were included:

- (1) clarification of production mechanism of secondary particulates through field observations to construct a simulation model of secondary particulates,
- (2) development of sub-diffusion models for low level emission sources such as automobile exhaust particulates, road dust, dust from piling yard, etc., and
- (3) development of sub-diffusion models for natural emission sources such as marine aerosols and resuspension dust.

In this fiscal year, the year of completion, field surveys of environmental concentration of SPs and meteorological conditions were carried out in the southern Kanto Plain in early winter to obtain very typical data available for the verification of the newly developed simulation model. The configuration of the measurements followed those of the previous year. Namely, particulates samplers and meteorological instruments were located from a vessel on Tokyo Bay to Kumagaya, 70 km northwest of the bayshore, and at the top of Mt. Tsukuba, 70 km northeast of the bayshore.

Intensified observation periods were held during 26 - 27 November and

6 - 7 December 1991. Very high levels of NO_x and SPs were observed during the both periods under the expected weather conditions characteristic in early winter in this district.

The field data obtained from the three-dimensional observations of air pollution and meteorological factors in summer of the first and second years and in early winter of the third through fifth years include a lot of valuable information, and provide bases of further development of the researches of local air pollution.

The most important finding in the summertime observation is that the urban effect, especially its thermal effect, is significantly large on the processes of inland penetration of the sea breeze and the enhancement in the pollutant concentrations.

In the observations performed in three early winter seasons, the high concentrations of NO_x and SPs were investigated in relation to the characteristics of local front frequently lying over the south Kanto district and the stagnant region on the north of the front. Through a statistical analysis, it was elucidated that the local front and the stagnant region are formed under the strong influence of the mountainous region on the west of the Kanto Plain.

Data analysis of the diffusion experiment using real-scale buildings to investigate their mechanical effect on air flows proceeded. It has been found that the so-called roof vortex in the street canyon had more complicated structure than was identified by visualization with smoke.

The simulation model for the environmental concentration of SPs has been constructed after the inclusion of the secondary particulates from SO₄²⁻ and NO₃⁻, influence of moisture and Cl⁻ in addition to the emission of simple particulates. In the past simulation study for SPs, calculated concentrations were always smaller than the measured ambient data. In addition, it was known that the measured concentrations tended to increase when the relative humidity had large values. This does not indicate a defect of the measuring techniques but a nature of SPs. Therefore, the inclusion of the moisture effect gives a reasonable coincidence between the calculated and measured concentration levels. Furthermore, the large contribution of Cl⁻ was an important result of the field observation, although its emission source is still uncertain.

Concentration of SPs under various meteorological conditions can be predicted when the present simulation model is connected with the meso-scale weather and transport model already developed.

30. Efficient Treatment of Offensive Odors by Using
Functional Polymeric Materials and Microorganisms
(I) Deodorization by Using Polymeric Materials
(FY 1988 - 1991)

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The offensive odors consist of many kinds of component. The concentration of the odorous materials is very rarefied in the air. Therefore, the treatment of offensive odor is very difficult. For preserving the comfortable urban amenity, it should be urgent to develop a novel, small-sized, efficient and economical system for offensive odor treatments by using various functional polymeric materials and microorganisms.

In the fiscal year 1991, following subject matters were studied.

1) Preparation of fibrous polymeric adsorbents for deodorization.

For developing the fibrous polymeric adsorbents for deodorization, various fibers were finished with chemicals having the deodorizing function. These fibrous adsorbents have an excellent deodorizing ability for ammonia. The durability is fairly good.

2) Preparation of polymer catalyst for deodorization.

A new polymer catalyst prepared from colloidal gold fixed on fiber was confirmed to be effective for light-induced oxidation of hydrogen sulfide in the air.

3) Preparation of porous hollow fiber for separating and concentrating the odorous materials.

Wet spinning of poly(sulfone) hollow fiber was investigated by using the fourfold coaxial spinning nozzle. The porous structure of the hollow fiber depended on the coagulation speed of poly(sulfone) dope in the coagulation bath. The controlling technique of the porous structure was developed.

4) Preparation of pervaporation membrane for separation of offensive odorous materials.

The membranes for the separation of offensive odors were prepared by using plasma polymerization of fluorocarbon on porous poly(propylene) membrane. Separation coefficient of the membrane for trimethylamine and methyl sulfide is 150 and 200, respectively. We tried to produce mini-module with the separation membranes and examined it by two kinds of separation modes from a practical point of view. Those are the continuous and the periodical permeate-sampling modes. In both separation modes, separation performance, particularly separation coefficient, was much improved

than that in normal pervaporation modes.

5) Design of deodorizing system using the functional polymeric materials.

Deodorizing systems using the functional polymeric materials that were developed in the study were designed. For biological deodorization, new support combining porous hollow fiber with fiber for immobilizing microorganisms was applied. For chemical deodorization, new fibrous polymer catalyst was applied. Miniaturization and energy saving of deodorizing system will be expected by using these materials.

30-II. Efficient Treatment of Offensive Odors by Using Functional
Polymeric Materials and Microorganisms
(II) Biological Deodorization
(FY 1988-1991)

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Biological deodorizing processes have drawn attention in view of their lower operating costs as compared to physical or chemical processes such as washing with chemicals, absorption with activated carbon and incineration; and have been increasingly adopted in facilities for night soil and sewage treatment. However, their removal efficiency for sulfur-containing malodorous compounds is reported to be poor.

The authors found that methyl mercaptan (MM), dimethyl sulfide (DMS), dimethyl disulfide, and hydrogen sulfide (H_2S) were efficiently removed from contaminated air by Thiobacillus thioparus TK-m. More than 99.99% of DMS was removed by this bacterium when the DMS load to the cells was less than 4.0 g/g (dry cell weight) per day. The maximum DMS load for acclimated activated sludge to obtain a 99.9% removal has reported to be 9.0 mg/g of mixed liquor suspended solids (MLSS) per day. Therefore, the cultures of T. thioparus TK-m removed DMS 440-fold more rapidly than did the acclimated activated sludge.

By the effective use of this bacterium, equipment capable of efficiently treating sulfur-containing malodorous gas is expected to be developed. In designing an apparatus to treat a large quantity of malodorous gas at a low concentration, a reduction in pressure loss in the apparatus is important to economize operating costs. The authors used a packed tower system that features a lower pressure loss and easier maintenance.

Cells of Thiobacillus thioparus TK-m were immobilized on cylindrical porous polypropylene pellets (5 mm ϕ x 5 mm) which were packed in an acrylic cylinder of 50 mm inner diameter up to the height of 800 mm. When a

sulfur-containing malodorous gas was charged to this packed tower at the superficial velocity of 0.1 m/s. maximum loading capacity (mmol/l/day) for a malodorous gas to attain the removal rate of 95% or more was: 3.66 for DMS, 8.75 for MM, and 17.37 for H_2S . At this time, the inlet concentration (ppm) of the malodorous compound was: 7.44 for DMS, 17.8 for MM, and 36.4 for H_2S . Next, a gas containing both DMS (2-16 ppm) and H_2S (60 ppm) was charged and it was found that treatment of the malodorous gas containing higher H_2S and lower DMS concentrations posed no problem. The influence of ammonia, which coexists with sulfur containing compounds in the malodorous gas from night soil treatment and others, was also examined. No inhibition by ammonia on the decomposability of DMS was observed. Thus, significant deodorizing effects were observed.

Then the authors constructed a pilot plant for treating the sulfur-based malodorous gases generated in sewage treatment. The pilot plant had two 20 cm diameter columns (packed towers), each about 4 m tall, which were packed with about 0.13 m^3 of porous ceramics having a particle diameter of about 2 cm. The malodorous gas, induced from the upper part of the dehydrator in the sewage treatment plant's dehydration chamber, was fed at about $0.75\text{ m}^3/\text{min}$ from the lower part of the columns. This gas contained roughly 50 ppm of H_2S and 5 ppm of MM. Measuring the concentrations of these two gas components at the column inlets and outlets showed that more than 98.5% of H_2S and more than 95% of MM were removed when the column pH was maintained between 6.0 and 7.5. The sulfur compounds in the malodorous gas were oxidized to sulfuric acid, which lowered the pH value inside the columns. Therefore water was passed through the columns intermittently to maintain the pH value. The treated sewage in this treatment plant was more suitable for the water passed through the columns than tap water because the treated sewage contained 20 mg/l of carbon dioxide and had the buffering ability against the addition of sulfuric acid.

31. Emission Control of Volatile Organic Halides by
Adsorption
(FY 1988-1991)

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The emission of organic halogenated compounds such as chlorofluorocarbons (referred to as CFCs) and chlorocarbons results in global and local environmental problems. Recent research of earth science concluded that the atmospheric CFCs, halons, and some chlorocarbons deplete the stratospheric ozone. In addition CFCs are presumed to have a global warming potential with the contribution of 24%, although CO₂ gives that of 55%. Furthermore, some chlorinated organics such as trichloroethylene, tetrachloroethylene, and carbon tetrachloride are toxic to human. Therefore, increased use of such halogenated compounds affects our environment directly and indirectly.

Technologies for protecting from those compounds are classified into three categories; (1) input control, i.e. alternative materials and process, (2) internal control, i.e. reduction of the use, and (3) output control, i.e. emission control by recycling and destruction. This classification is almost common to any other environmental problems including NO_x, SO₂, waste.

This research starting since the fiscal year of 1988 is a four-years program, aiming at establishment of recycling of the halogenated compounds by adsorption technology. The program of this research is divided into (1) development of new and effective adsorbents for the halogenated compounds, (2) development of desorption methods from adsorbed phase, and (3) proposal of prototype system of adsorption-desorption cycle. In the final year of 1991, results are summarized.

Regarding the development of adsorbents, adsorption of CFCs was investigated onto zeolites, an inorganic crystal. Zeolites modified by alkaline and alkaline earth metal ions gave S-shaped isotherms. All experimental isotherms of CFCs were satisfactorily explained in terms of Hill's adsorption equation, which accounts for

not only surface-molecule interaction but also adsorbed molecules interaction. Kinetic study on adsorption in continuous flow-type experiments indicated that overall mass transfer coefficient governing the adsorption varied as a function of CFC's molecular size, metal ion in zeolite, particle size of zeolite, gas velocity, shape of the adsorption curve (break-through curve).

Regarding desorption method, temperature-program desorption of CFCs adsorbed on zeolites at atmospheric pressure was influenced by CFC's molecular size, metal ion in zeolite, particle size of zeolite, flow rate of expelling gas, rate of temperature increase, etc. Pressurized desorption of trichloroethylene on an active carbon was also conducted using supercritical CO_2 at low temperature in the range of 40 to 80 °C. Both sufficient desorption and regeneration of the active carbon attained at temperature below 60 °C and at pressure below 200 kg/cm².

Regarding prototype system of adsorption-desorption cycle, we proposed a single column adsorption system, in which adsorbed molecules were desorbed by zone-heating method. The heater by microwave power rapidly moved from one end of the column to another end.

32-I. Catalytic Combustion Technique for Reduction of NO_x from Small Scale Stationary Sources

(FY 1989 - 1992)

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The air pollution caused by nitrogen oxides (NO_x) is one of the most serious environmental problems in large cities. NO_x from big scale stationary sources such as power plants is effectively removed by the ammonia catalytic reduction. On the other hand, NO_x from the small scale stationary sources such as small boilers and heaters is not removed at the present time. Therefore, the development of the technology for the reduction of NO_x from the small stationary sources is extremely desired now. The purpose of this study is to develop the high performance combustion catalyst. In order to develop the combustion catalyst, the thermal resistance of the catalyst must be improved.

We have already reported that an alumina synthesized from aluminium isopropoxide using 2-methylpentane-2,4-diol as a solvent showed a high surface area even after calcination at 1000°C and that the platinum catalyst using this alumina as the support also showed higher catalytic activity for the CO or CH₄ oxidation reaction. In the third year of the four-year research program, the role of organic complexing agents on the properties of alumina produced, especially specific surface areas and morphology, was mainly investigated. The thermal behavior, the size and the morphology of the alumina particles depended on the complexing abilities of the solvent used. The weaker complexing agents such as ethers and monohydric alcohols yielded the aluminas keeping a high surface area in the higher temperature region. In contrast, the stronger ones such as non-branched diols yielded aluminas crystallizing to α-phase at lower temperature. The medium complexing agents such as 2-methylpentane-2,4-diol gave aluminas with high specific surface areas in a wide range of temperature. These facts are elucidated by the difference in size and shape of precursor gel particles, which is due to prevention of particle growth by the complexing agent.

32. II Catalytic Combustion Technique for the Reduction
of NOx from Small Scale Stationary Sources
(FY 1989 ~ 1992)

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Although the air pollution circumstances in Japan are greatly improved recently, the NOx concentrations in the area of large cities keep still serious level. Consequently, it has been occurred the necessity of NOx regulation tightening for the small scale sources which had not regulated hitherto. Since the small scale combustion facility requires both a high economical efficiency and a small size, conventional NOx reduction techniques such as the catalytic reduction with ammonia injection are hardly applied. The use of catalytic combustors in place of conventional burners in small scale stationary combustion systems has shown significant advantages in the control of NOx emissions. The purpose of this project is to develop a low NOx catalytic combustor for the small scale stationary sources such as a boiler and a hot water supply system.

In order to analyze the catalytic combustion in a honeycomb monolith catalyst for the purpose of developing a low NOx small scale combustor, temperature measurements of wall surface in a working combustion catalyst has been carried out using the optical-fiber radiation thermometer. Instead of a standard sapphire radiation probe, the quartz probe of 0.25mm OD was developed. Measured temperature profiles indicate that the combustion reaction was limited in the region of upper stream side of catalyst at low gas velocity condition, and the reaction zone was extended to the downstream as the gas velocity was increased.

Experimental and theoretical studies of the combustion of C_3H_8 in the fluidized bed, using the platinum catalyst mixed with bed material, have been conducted. The objective of the study was to confirm the possibility of this combustion method, and to evaluate its combustion characteristics. Small fluidized bed combustor, in which the platinum catalyst mixed with alumina in the range of 2~8%, was used for the experiment. The catalytic combustion of C_3H_8 was easily started by the flame combustion in freeboard, and had over 90 % combustion efficiency at low temperature of 700K, at which the ordinary fluidized bed combustion of gaseous fuel was impossible. The combustion efficiency was easily improved up to 95% by the increase of the bed temperature, the catalyst content, or the static bed height. The bed temperature variation was negligible, therefore the catalyst for this method could be developed for the narrow and specific temperature range.

32 III Catalytic Combustion Technique for the Reduction of NOx from
Small Scale Stationary Sources
(FY 1989-1992)

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Global environmental pollution such as acid rains caused by NOx is being recognized as serious problem. The source of NOx is combustion which is utilized in automobiles, power plants, boilers and so on. There are two types of NOx. One is fuel NOx formed in the combustion of nitrogen-contained fuels. Other is thermal NOx formed by the reaction of N₂ with O₂ in air at the temperatures above 1500 °C. In the ordinary flame combustion, the thermal NOx can not be depressed because the flame temperature is above 1500 °C. NOx from the big scale stationary source such as power plants is removed by ammonia catalytic reduction method. However, NOx from the small scale stationary sources such as small boilers and water heater is exhausted as it is.

Combustion, which fuel gases such as H₂ and CH₄ contact with O₂ on the surface of catalysts, is called catalytic combustion. In this combustion, combustion temperature can be controlled by the concentration of the fuel gas and O₂ below 1500 °C. However, the practical combustion catalyst which can be used at the temperature above 1000 °C is not developed.

In this project, in order to reduce NOx from small scale sources, our purpose is to develop the combustion catalyst containing of SiC as supports or structural materials. SiC has high potentiality as supports or structural materials of combustion catalysts because it is stable up to 1650 °C physically and chemically in inert gases. We have developed SiC-Si composite which is stable at 1300 °C in oxidizing atmosphere in this project. SiC produced from rice hulls was porous and excellent component of the SiC-Si composite. The SiC-Si composite is expected to use as supports or structural materials of high-temperature combustion catalysts. Another purpose of this project is to establish recovery and recycle method of the waste combustion catalyst by chlorination in order to develop economical combustion catalysts. SiC and Si metal in the waste catalyst will be

converted to SiCl_4 by chlorination. SiCl_4 can be used as the raw materials of fine ceramics and organic silicon compounds.

In the fiscal year 1991, following subject matters were studied.

- (1) Development of supports or structural materials of combustion catalysts having thermal shock resistance property. The thermal shock resistance property is important for combustion catalysts of small scale combustor because of repetition of ignition and extinguishing.
- (2) Reaction rates of chlorination of SiC-Si composite supports or structural materials of catalysts.

The results in 1991 are summarized as shown below:

- (1) The crack was not observed on the surface of SiC-Si composite pellets given thermal shock of $3400^\circ\text{C} / \text{sec}$ from 1300°C to 20°C in oxidizing atmosphere. The SiC-Si composite pellets had high thermal shock resistance property.
- (2) SiC-Si composite disks were produced from rice hull SiC powders and Si metal powders by plasma activated sintering method. The composite disks were able to be processed mechanically, but were easy to be oxidized at 1300°C in air.
- (3) The SiC-Si composite disks processed to honeycomb shape mechanically were treated at 1500°C in argon. The honeycomb composite disks were able to suppress oxidation at 1300°C in air. The coating layer of $\text{BaAl}_{12}\text{O}_{19}$, which have a large surface area at elevated temperatures, on the surface of the honeycomb disks was strong mechanically and did not fall off the disks at 1300°C in oxidizing atmosphere.
- (4) From the results of the chlorination rate of rice hull SiC-Si composite pellets, all Si component was chlorinated to SiCl_4 at 900°C for 1 hr.

33. Evaluation and Control of SOF from Diesel Engines
(FY 1989-1991)

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In regard to the problem of atmospheric pollution by diesel motored vehicles, reduction of nitric oxides in the exhaust has been the main concern. Along with this, the emission of particulate matter is becoming a serious problem, because it contains Soluble Organic Fraction (SOF), which is suspected to cause severe biological effects.

This study concentrates on the development of rapid and separative measuring methods of dry soot and SOF, and on the analysis of combustion conditions which relate to SOF formation inside the combustion chamber. The results obtained in the 3 years research program, FY 1989-1991, are summarized as follows:

1) Development of a rapid measuring method of SOF in the diesel exhaust

Filter collection method using dilution tunnel is usually employed to measure the mass concentration of particulate in the diesel exhaust gas. In this subtheme, the accuracy of the method was improved by keeping the filter temperature constant to reduce the effect of sampling gas temperature on the collected particulate mass, then it was employed as a standard method to examine the other methods developed and used in the research.

Accuracy and transient response of TEOM (Tapered Element Oscillating Microbalance) was checked against both of the standard method and an opacimeter. The tests showed that TEOM is a useful device for rapid and continuous measurement of particulate matter.

A multiple detection opacimeter was developed, and confirmed of its performance. It provides with improved sensitivity, reduced noise and expanded limit for low density smoke compared to conventional opacimeters.

These investigations enabled continuous measurement of particulate concentration which conventional intermittent measuring methods are not capable of, and evaluation of transient particulate emission characteristics of diesel engines and diesel particulate traps became practicable.

2) Analysis of combustion conditions for the reduction of SOF

A simple, non-dilution sampling system was employed in this subtheme for the separative measurement of SOF and dry soot. This system extracts diesel exhaust gas from the exhaust manifold and leads it directly to a filter. After several improvements, the method was proved to be reliable for SOF/dry soot measurement under steady-state engine operation. SOF measurements and exhaust gas analyses were carried out with varied engine speeds, loads, injection timings and intake port specifications. The analyses clarified influences of engine load, excess air ratio, exhaust gas temperature and hydrocarbon emission on SOF emission.

One of the experiments, in which the intake system was changed from dual (original) to single port, implied the effect of enhanced turbulence on SOF reduction. Then, the potential of intake port and combustion chamber design to increase turbulence was investigated by in-cylinder LDV data. It was proved, however, that minor modification of these specifications increases the turbulent intensity little.

Also, CARS (Coherent Anti-Stokes Raman Spectroscopy) measurement of gas temperature was planned to investigate the relationship between combustion gas temperature and SOF emission. It had not reached to the stage of measurement in engines, but fundamental experiments using high pressure/ high temperature vessel proved that favorable accuracy is obtainable in the temperature measurement of gases with the pressure from the atmospheric to 3 MPa.

34. Study on the treatment of toxic gases
(FY 1991 - 1994)

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Organic solvents used in various industries pollute not only the atmosphere of factories but also the air in the vicinity of the factories. The number of gases used for special purposes like those used in semiconductor industry are increasing and most of them are toxic. These solvents and gases can be hardly treated by conventional methods. In this research we develop a new method for efficient degradation of toxic solvents and gases. Degradation is conducted by the illumination with deep UV light. Final and intermediate degradation products are identified, and the treatment of toxic degradation products is studied to complete this method. The mechanism of the photolysis is also studied on the basis of the identification of degradation products.

Three halogenated organic gaseous compounds, 1,2,2-trichloro-1,1,2-trifluoroethane(R113), trichlorofluoromethane(R11) and 1,1,1-trichloroethane, were degraded by the illumination with 43 W low pressure mercury lamp whose light bulb is made from spracil. Three of them were degraded quite rapidly. Photolysis reaction follows the first order kinetics. CO_2 was formed almost spontaneously with the degradation. As final degradation products C^- and F^- were produced besides CO_2 . Several small amount of intermediate products were formed. Most of them are organic acids. Acetic acid was detected as an intermediate product for the degradation of 1,1,1-trichloroethane. These intermediate products were degraded completely by the continuation of illumination.

35. Study on Hybridized Catalytic System for Diesel NO_x
Removal (1)
(FY 1991-1995)

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Atmospheric pollution by nitrogen oxides (NO_x) emitted from diesel vehicles is in a serious situation in Japan. This research aims at the development of a practical NO_x removal system by combining advanced catalytic techniques to decompose or reduce NO_x with soot, CO and hydrocarbons.

In the beginning year of the five-year research program, National Institute for Resources and Environment conducted following three major researches.

(1) Catalytic properties, especially O₂ adsorption and desorption characteristics, of Pd/Mg oxide catalysts were investigated. Using Pd/MgO as the model catalyst, temperature programmed O₂ desorption and temperature programmed oxidation experiments were conducted. It was found that the reduced Pd supported on Mg containing oxides released adsorbed oxygen at relatively low temperatures, was resistant to bulk oxidation at high temperatures. Such catalysts may be effective to NO decomposition.

(2) Mechanism of the selective catalytic reduction of NO by hydrocarbons was investigated. Carbonaceous radicals and deposits were found to be formed on the catalyst surface during the reaction on gamma-alumina. The deposits acted as selective reducing agents on raising the temperature. The results indicate that both the carbonaceous radical and the carbon deposits play a

crucial role, perhaps as intermediates, in the selective reduction. The radical was likely to be produced from the carbon deposits through partial oxidation with O_2 . The role of the catalyst was considered to promote the formation of carbon deposits from the reactant organic compounds by cracking or partial oxidation, to produce and stabilize carbonaceous radicals perhaps on Lewis-acid sites. The selective reduction of NO seemed to proceed through a radical reaction.

(3) Simultaneous reduction of NO_x and particulates was attempted by using foam-type filter traps with transition metal catalysts. The filter used had a particulate collection efficiency of 70% and was able to collect soot repeatedly after regeneration at $500^\circ C$. Decrease in the sulfur content in the fuel had no effect on the collection efficiency or on regeneration temperature. The filter trap with the catalyst had a certain activity for NO_x reduction but the activity dropped in a short period. Further study is needed on reduction of regeneration temperature and promotion of NO_x removal efficiency.

35. Study on Hybridized Catalytic System for Diesel NO_x Removal (2)
(FY 1991-1995)

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The air pollution by nitrogen oxides (NO_x) is a serious environmental problem in the urban areas of Japan. This is mainly because of the increase in the amount of NO_x emitted from diesel vehicles. In addition, the number of cogeneration systems using stationary diesel engines is increasing, which also emit considerable amounts of NO_x. However, no effective measures have been developed for the control of diesel NO_x.

This project, which just started in this year, aims at developing hybridized catalytic systems for removing NO_x emitted from diesel engines. The National Chemical Laboratory for Industry is in charge of R&D of catalytic methods to reduce diesel NO_x by using hydrocarbons. We have recently found that the selective catalytic reduction of NO by hydrocarbons is the most hopeful de-NO_x reaction. R&D of NO_x concentration with adsorbents or absorbents is the other target of the study with the intention of improving de-NO_x efficiency.

In this fiscal year, as the first year of the project, improvement of catalytic activities for the selective reduction of NO by hydrocarbon was mainly attempted. Basic researches were also conducted to obtain fundamental information on the de-NO_x reaction.

Since alumina is the highest active catalyst among metal oxides, various characteristics of the NO reduction over alumina were examined. Among various alumina catalysts prepared by different methods, pure alumina including little impurities showed relatively high activity. A striking feature of the selective NO reduction is that the reduction is promoted by the presence of oxygen. The efficiency of the reducing agent for NO reduction at low temperature increased in the following order, methane < propane < propylene < alcohols, indicating that hydrocarbons and oxygen-containing organic compounds liable to oxidation are good reducing agents at low temperatures. It was also found that the reduction of NO₂ occurred more

easily than that of NO.

Next, the effect of transition metals as catalyst component on the catalytic activities was investigated. In the case of ion-exchanged ZSM-5 zeolites, the activity of H-ZSM-5 was higher than that of Cu-ZSM-5 containing copper as a transition metal, under the conditions of low space velocity, high temperature, low hydrocarbon concentration, and vice versa.

This effect of transition metals was also observed for alumina-based catalysts, namely, the activity of alumina at low temperature and high space velocity was enhanced by supporting transition metals such as Co, Cu, Fe, Ni, Mn, and noble metals. The performance of Co/alumina catalysts depended on the cobalt sources and calcination temperature. Co/alumina prepared from cobalt acetate and calcined at temperatures higher than 600°C showed excellent NO reduction activities, while Co/alumina prepared from cobalt nitrate and calcined at 500°C promoted only the oxidation of hydrocarbon, showing no activity for NO reduction. The supported cobalt species was found to be responsible for the activity difference.

The selective NO reduction was considered to proceed via partial oxidation of hydrocarbon or oxidation of NO to NO₂. The effect of coexisting oxygen and transition metals as the catalyst component is probably related to these two reaction steps.

Finally, the catalytic activities of several sulfuric acid-treated metal oxides were investigated, since solid acidity seemed to be one of the major factors to determine the catalytic performance. When titania and zirconia were treated with sulfuric acid in their preparation procedures, increase in the catalytic activity and selectivity was observed. This improvement of catalytic performance was attributed not only to the increase in surface area but also to the change of catalytic acidity. In the case of iron oxide, the treatment also promoted the activity for selective NO reduction. However, the treatment of alumina with sulfuric acid resulted in the decrease of catalytic activity, although NO conversion to N₂ increased at a low temperature such as 300°C.

35. Study on Hybridized Catalytic System for NO_x Removal (3)

(FY 1991 - 1995)

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Nitrogen oxides (NO_x; NO and NO₂) is one of the serious problems in the atmospheric pollution. Especially, reducing NO_x emission from diesel-powered vehicles is very difficult and it is necessary to develop innovative technologies. The aim of this research is the development of the catalytic technologies for removing NO_x emitted from diesel engines, such as buses and trucks. And we research the catalyst for reduction of NO by CO at low temperature.

In the first year of this research program, it was carried out that preliminary exploitation experiments of reduction of NO by CO over supported gold catalysts.

(1) Preparation of supported gold catalysts

Supported gold catalysts were prepared by coprecipitation method. These catalysts have the structure which high dispersed gold particles are supported over metal oxide. The diameter of these gold particles is about 4 nm.

(2) Reduction of NO by CO over supported gold catalyst

Catalytic tests were carried out in a fixed bed flow reactor and reaction condition are as follows, reaction gas ; NO(0.1%) + CO(0.1%) / He, space velocity ; 20,000 ml h⁻¹g-cat⁻¹.

Reaction of NO by CO proceeds as follows,



Au/α-Fe₂O₃ is most active in the gold catalysts which supported on simple metal oxides. The reduction of NO occurs even at room temperature and NO converts to N₂O. The formation to N₂ carried out at 150 °C and inlet NO almost converts to N₂ at 200 °C. The gold particles enhance the catalytic activity of the reduction of NO to N₂.

For the supports, α-Fe₂O₃ is good and when it was replaced by ferrites of Ni or Co (NiFe₂O₄, CoFe₂O₄), the activity is so noticeably increased. The abrupt increase of selectivity to N₂ takes place in the range from 50 to 80 °C for these catalysts. Comparing with the supported noble metal catalysts such

as Pt, Rh and Pd catalysts, supported gold catalysts are superior for the low temperature CO + NO reaction.

(3) Effects of moisture

There are moisture and oxygen in the exhaust gas from diesel engines. Non-supported metal oxides such as α -Fe₂O₃, NiFe₂O₄ and CoFe₂O₄, were appreciably deactivated by moisture in our experiments. It is reported that the suppression of N₂ formation by moisture is also observed in the case of supported Pt catalysts. On the other hand, when gold is supported on ferrites, some of the gold catalysts, for example, Au/ α -Fe₂O₃ and Au/CoFe₂O₄, maintain the conversion of NO and the selectivity to N₂ in the presence of moisture.

(4) Future tasks

This research showed that supported gold catalysts are active for the low temperature reduction of NO by CO, and Au/CoFe₂O₄ has the tolerance to moisture. Oxygen in the exhaust gas reacts with CO and it is expected that CO + O₂ reaction completes CO + NO reaction. Our further research should be focused on the selective reaction of CO with NO in the presence of excess oxygen.

36. Simultaneous Control Techniques of N₂O and NO_x from Coal Combustion (I)
(FY 1991 ~ 1994)

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Nitrous oxides(N₂O) is one kind of pollutants causing the global environmental problem, because it is one kind of green house effect gases and it has destructive effects to the stratospheric ozone layer as well as freon gas. In order to control simultaneously the emission of N₂O and nitrogen oxides(NO_x) from coal combustion, the following studies have been carried out in this research program.

1. N₂O formation and destruction mechanisms
2. The flowing conditions of solid particles in fluidized bed
3. Simultaneous control of N₂O and NO_x from pulverized coal combustion

1. N₂O formation and destruction mechanisms

The reaction of nitric oxide(NO) and N₂O formation in the nitrogen-oxygen system was investigated behind incident shock wave over the temperature range 3200-4000K. The experimental results could not be explained by Zeldovich mechanism. However, the simulation was found to be fairly consistent with the experiment by adopting following reaction.



To solve these problems more detailed experimental research is required.

In order to know mechanisms of N₂O formation and destruction in circulating fluidized bed combustion(CFBC) conditions, heterogeneous reactions between char, CaO and gases were studied. To simulate the N₂O formation in CFBCs, a batch combustion reactor was used. The results show that N₂O emission characteristics in CFBCs are well explained in a batch reactor. In order to investigate the effects of the partial devolatilization, the char prepared at various devolatilization temperatures was burnt. N₂O emission is strongly dependent on the devolatilization temperature. The char devolatilized at higher

temperature showed the lower N₂O formation. N₂O formation starts at the early stage of the combustion and continues in relatively long period. This formation reaction mostly takes place in the gas phase. These results suggest that the contribution of the partially devolatilized char on N₂O formation is considerably large in CFBC. Reduction activities of the solid particles on N₂O and NO were measured. CaO shows higher N₂O reduction activity. N₂O reduction rate is always faster than that of NO for same particle.

2. The flowing conditions of solid particles in fluidized bed

Solid particles flowing in a circulating fluidized bed was visualized by using a penetrative type particles image scope and a reflective type optical fiber probe. Local solid holdup and its variation were measured. Dilute and denser phases were passing at the tip of the probes alternately. Concentration of the denser phase increased with the increase of the solid circulating rate or the decrease of the gas velocity. The reflective optical fiber probe could be used to monitor local mass flux or solid holdup. Also, optical fiber probe could be applied pressurized fluidized bed at least up to 5.0 MPa.

3. Simultaneous control of N₂O and NO_x from pulverized coal combustion

The experiments of pulverized coal combustion have been carried out to estimate the N₂O and NO_x emissions. A down-fired 40 cm ID tunnel furnace was used in this study. It allows a firing rate of 10 kg-coal/hr. In the combustion of Taiheiyo coal(Japanese coal), the flue gas N₂O concentration was between 2 and 3 ppm at the conditions of high flue gas O₂ concentration.

36. Simultaneous Control Techniques of N_2O and NO_x from Coal Combustion (II)
(FY 1991 ~ 1994)

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The objective of this research project is to develop suitable combustion technology for simultaneous abatement of nitrogen and nitrous oxides (NO_x and N_2O) emissions from bubbling and circulating fluidized-bed coal combustors. For understanding mechanism of NO_x and N_2O formation, combustion experiments under various operating conditions are made with both types of experimental fluidized bed combustors.

1. Bubbling fluidized bed combustor

An experimental combustor having an inner diameter of 0.16 m and a height of 3 m was designed and constructed for measurement of NO_x and N_2O emission levels. A heat exchanger tube immersed in the fluidized bed was used for controlling combustion temperature. Continuous gas analyses were made by means of infrared rays for NO and N_2O and magnetic force for O_2 . Preliminary combustion experiments of sub-bituminous Taiheyo coal were performed to confirm steady state operation and to measure NO and N_2O emission levels. Excellent performance for controlling bed temperature has been confirmed through the experiments. In case of single-stage combustion scheme, both emission levels of NO and N_2O increased with stoichiometric air ratio and were respectively ca. 300 and 30 ppm at 850 °C and the air ratio of 1.2.

2. Circulating fluidized bed combustor

An experimental circulating fluidized bed combustor was constructed. The combustor had a riser reactor of 0.1 m inner diameter and 6 m high and moving bed downcomer for solid recirculation into the riser. An L-valve system was designed for controlling solid circulation rate. Although the L-valve system had a little difficulty to keep a constant solid circulation rate, stable operation was successfully conducted by changing air flow rate into the horizontal tube of the valve. N_2O emission level at 850 °C was ca. 100 ppm and was markedly higher than that from the bubbling fluidized bed combustor as mentioned above.

37. Air Pollution Control of Automobile Exhaust Gas
in Urban Road Tunnels
(FY 1991-1996)

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In the metropolitan regions, the environmental concentrations of the nitrogen oxides (NO_x) and particulate materials (PM) rise considerably and exceed the standard value in the majority of the measurement stations near the road way. Specially, the concentrations rise at near the outlets of road tunnels and ventilation towers. Diesel engine vehicles emit more NO_x and PM than gasoline engine vehicles, and these substances at high concentration levels are an irritant and a health concern. Therefore, the air quality control of road tunnels is very important. The removals of NO_x and PM are required to keep air quality within acceptable levels on urban area. However, the removals of these contaminants are very difficult at low concentration levels in road tunnels.

Our research purposes are two of the following. One is to find an oxidizing method to change gaseous species NO_x into organic nitrates to remove by the absorb filters easily. Another is to evaluate the impact of NO_x and PM removal device.

1). Many experimental for simultaneous removal of NO_x and PM have to carry out by using different reactor devices. The test gas mixtures are NO of 0.8 to 1.5 ppm diluted from high concentration gas of 4797 ppm nitric oxide (NO) in cylinder by room air and NO_x of 1 to 1.8 ppm from Diesel-engine exhaust. For addition of ozone amounts 7.3 ppm, the convert ratio of NO to NO₂ was about 99 % for cylinder NO and Diesel exhaust (Fig.1). From the results depend on running of electric collector, in the both cases of cylinder and exhaust gases, the removal efficiencies of PM have been about 82 to 92 % of the PM amounts at inlet. The PM removal efficiencies were sufficiently for Diesel exhaust particulates of 0.1 μ m diameter. The fine particulates, as a soluble organic solvent in Diesel exhaust, may be proposed to be used as an absorbent for NO_x removal from tunnel gases.

2). For air quality management of road tunnels, one-dimensional steady-state mass balance models have been performed. The concentrations of

CO, NOx and PM are governed by the following tunnel characteristics, one way traffic direction, length of tunnel 3000m, velocity of passing vehicles 60km/hour, longitudinal air velocity 8.3m/sec, traffic volume 2659 vehicles /hour and performance of the removal devices, 0.5 ppm (for NOx), 80% (for PM), respectively. The simulator developed by personal computer programing was very useful for detailed evaluation of air quality in tunnels and electric energy cost. For the performance 0.5 ppm of NOx removal devices and in the case of forced condition of last device, the removal efficiency of NOx is about 70% of exhaust amounts, then the average concentration of NOx has to be controlled less than 0.8 ppm in the tunnel. The running cost of removal devices is about thirty thousand yen/hour/km (Fig.2).

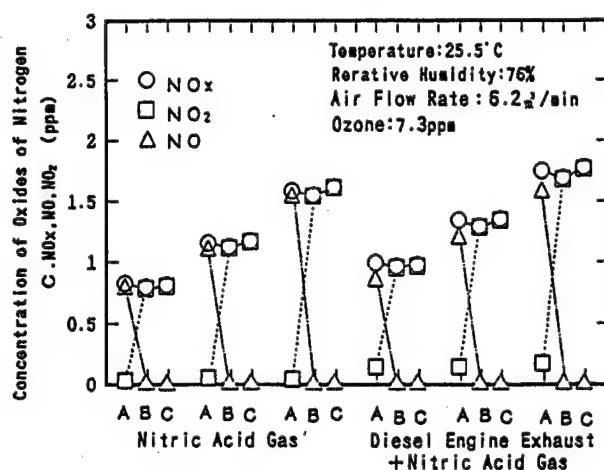


Fig.1. Effects of addition of ozone and running of electric particulates collector

A: test gas mixtures B: addition of ozone C: running of electric collector

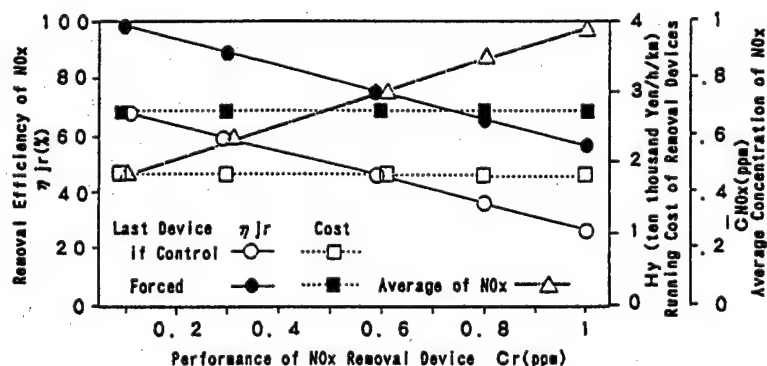


Fig.2. Removal efficiencies of NOx, running costs and average concentrations of NOx correspond to performance of NOx removal devices

38. Effective Treatment of Hazardous Chemicals by
Ecological Control of Activated Sludge
(FY 1988 - 1992)

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In the field of pollution control in aquatic environment, organic pollutants which can be detected as general indices of water qualities such as biological oxygen demand (BOD), chemical oxygen demand (COD) and suspended solids (SS) have been reduced from waste water by conventional biological treatments. On the other hand, it has come out a new type of pollution by hazardous chemicals which had been left behind the problems of BOD reduction.

It is not easy to decompose the hazardous chemicals by biological treatment, because that has been developed for reducing the ready decomposable components such as BOD-substances. To overcome such a limitation, a new technique to enhance the ability of microorganisms to degrade hazardous chemicals should be required.

To eliminate hazardous chemicals by a biological waste water treatment process, microorganisms capable to decompose the chemicals should be acclimated to it and retained suitably in the reactor of the treatment system. Several techniques have been applied to hold the adapted microbes in the reactor; immobilization by chemicals means, by carrier, or retaining by membrane separation method.

The aim of this study is to find a proper method for reduction of hazardous chemicals by physiological and ecological way to enrichment and enhancement of microbes active for the chemicals in the activated sludge.

In FY 1991, effect of continuous and batch operations in the

activated sludge process on its adaptability to para-nitrophenol (PNP) was studied. Continuous and batch activated sludge were applied to degradation of PNP. A seed activated sludge preliminarily acclimated to aniline was fed with synthetic waste water containing PNP of 50 mg/l for continuous activated sludge reactor (CAS), connected to a membrane separation module, and 200 mg/l for batch activated sludge reactor (BAS), respectively. After 3 months of acclimation to PNP medium, PNP in the influent was removed constantly in both CAS and BAS reactors. According to PNP degradation rates estimated, maximum velocity of PNP decomposition (V_{max}) in CAS was $1/4$ of that in BAS, and saturation constant (K_m) to PNP in BAS was 6 times higher than that in CAS. When PNP loaded was higher than that at V_{max} , PNP acted inhibitory to both CAS and BAS sludges, PNP degradation velocity declined sharply in CAS. It was suggested that different operation of activated sludge treatment made two types of acclimated sludge based on PNP utilization of bacteria dominant in each system.

39. Treatment of Chemicals in Waste Water by Supercritical Fluid
(FY 1988 ~ 1991)

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The diffusion and the accumulation of chemicals in the environment has been recognized as one of the most important environmental problems, so the development of effective processes designated to remove priority pollutants and other non-biodegradable organics from industrial waste water is in significant demand.

Supercritical fluid offers excellent potential as process solvents in chemical and environmental engineering applications, because of its particular properties. The objective of this study is to develop the technique to remove chemicals by supercritical fluid. The following articles are the substances of this study.

1. Measurement of phase equilibrium

The apparatus to measure phase equilibrium is designed and produced. By the use of this apparatus, the phase equilibria for chemicals in the supercritical Carbon Dioxide are measured.

2. Development of the process combined with concentrator

Chemicals in waste water are treated by two steps of the process. At first, the chemicals are removed from the waste water by concentrator, for example adsorbent. Secondly the chemicals in the concentrator are extracted by supercritical fluid, and simultaneously the concentrator is regenerated.

3. Development of countercurrent process

Chemicals in waste water are directly extracted by supercritical fluid using countercurrent equipment.

In FY 1991, article 2 and 3 were studied. In article 2, the regenerations of the activated carbons loaded with aromatic nitro compounds and with Polyoxyethylenenonylphenylether (POE, nonionic surface-active agent), by supercritical Carbon Dioxide were researched. In article 3, the removals of Nitro Benzene (NB), Ortho Nitro Toluene (ONT) and Ortho Nitro Phenol (ONP) from aqueous solutions directly by supercritical Carbon

Dioxide were researched.

In the case of the regeneration of the activated carbon loaded with NB, the velocity of the regeneration of the pores of radius less than 10 Å was found to be smaller than those of radius of 10 ~ 30 Å. The regenerated fraction calculated with the specific surface area of regenerated activated carbon measured by N_2 adsorption was smaller than that calculated with NB amount adsorbed from NB aqueous solution. This was considered to be caused by the fact that N_2 could enter into the pore of activated carbon more easily than NB in aqueous solution. Above the pressure of 200 kg/cm², the regenerated fraction increased as temperature increased, but below 150 kg/cm², the fraction decreased reversely as temperature increased. The reversal was considered to be caused by the reversal of the effect of temperature on the solubility of NB in supercritical Carbon Dioxide.

In the case of the regeneration of the activated carbon loaded with POE, the regenerated fraction was smaller than that of NB loaded activated carbon for the same condition of regeneration. The ultraviolet and visible spectrum of POE in supercritical Carbon Dioxide was similar to that in aqueous solution. The spectrum of aqueous solution of extracted POE precipitated in glass trap was similar to that of reagent POE which had been used to make POE loaded activated carbon sample at the beginning. So, POE extraction was known not to be accompanied with chemical change. At the temperature of 35 °C, the regeneration proceeded remarkably above the pressure of 100 kg/cm², and at the temperature of 50 °C, the regeneration proceeded remarkably above the pressure of 150 kg/cm².

As for the removal of aromatic nitro compound from aqueous solution directly by the use of the countercurrent equipment, 100 ppm of NB, ONT and ONP aqueous solutions were researched and compared, at the temperature of 35 °C and the pressure of 100 kg/cm². NB and ONT were found to be removed analogously. When the space velocity for the feeding of these aqueous samples were 1.5 (SV 1.5 : contact time 40 minutes), and the feeding ratios of supercritical Carbon Dioxide to aqueous samples were 0.6, almost NB or ONT were removed from the effluents. In the case of the treatment of 100 ppm of ONP aqueous solution by SV 1.5, almost ONP was removed from the effluent when the feeding ratio of supercritical Carbon Dioxide to aqueous sample was 1.0.

40. Study on the New Advanced Techniques for Treatment of Waste-Waters Containing Hazardous Substances from High-Technology Industries (FY 1990-1993)

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Waste-waters containing toxic substances such as arsenic-, antimony, and fluorine-compounds, used in a large quantity in the high-technology industries, have been treated so far by the aluminum sulfate method, the flocculation with polymer flocculants and coprecipitation with lime. However, these methods show so low removal efficiencies that the attainment to the emission standard for waste-waters is difficult by using them. Furthermore, the above treatment methods have disadvantages including increase of the salt concentration in treated water and formation of sludges with dehydration resistant properties. The present work aims to develop the method for the effective removal of toxic substances in water by giving the selectivity for toxic substances to materials which are stable in the water. For that purpose, chelating resins and active metal oxides with high selectivity, large absorption capacities, and high distribution coefficients for arsenic, antimony, or fluorine will be developed. By establishing the treatment process of waste-water by use of these adsorbents, it will be demonstrated that the toxic substances in waste-water from high-technology factories are surely removed, and miniaturized treatment apparatuses will be developed. The following was investigated in the 1991 FY.

1. Development of high performance chelating resins

Diphenylthiocarbazone resin (Dz-resin) containing nitrogen and sulfur atoms as a coordinating atom and 3-phenyl-5-mercapto-1,3,4-thiazole-2thion resin (Bismu-resin) containing two sulfur atoms as a coordinating atom were synthesized and the adsorbabilities of various metal ions to these resins were examined. Both the resins were found to show a high adsorbability and a high separation factor to antimony(III) and to hardly adsorb arsenic(III). Therefore we tried to prepare different resins to develop chelating resins capable of adsorbing and recovering both arsenic(III) and antimony(III) simultaneously and selectively.

The chelating resin (Thionalide-resin) was prepared by impregnating a porous resin with an 2-mercapto-N-2-naphthyl-amidoacetate compound, which coordinates with sulfur and oxygen atoms, as ligand and then the adsorbabilities of various kinds of metal ions (copper(II), cadmium(II), zinc(II), antimony(III), arsenic(III), lead(II), and iron(III)) to the

resin obtained was investigated. The adsorbabilities of the metal ions tested to Thionalide-resin were found to vary markedly with pH of the solution. Thus at pH more than 5 relatively many metal ions such as copper(II), cadmium(II), zinc(II), antimony(III), arsenic(III), and lead(II) were adsorbed almost 100% on Thionalide-resin. However, at pH 0 - 1.5, only copper(II), arsenic(III) and antimony(III) were adsorbed selectively and with 100% efficiency, and the very high exchange capacity were found for these metal ions; 45.0 mmol/g for arsenic(III), 15.0 for antimony(III), and 50.0 for copper(II). Because the pH of the raw water (gallium-arsenic system) from the factories of high technology is strongly acidic (pH 1 - 2.5), the present resin can catch and recover directly arsenic(III) and antimony(III) from the waste water above. Thionalide-resin is therefore considered an extremely ideal adsorbent.

2. Removal of fluoride ion.

2.1 Suppression of interference from metal ions in fluoride determination by ion chromatography.

The existence of aluminum(III), iron(II), calcium(II), cerium(III), cerium(IV), lanthanum(III), yttrium(III) ions interfered with determination of fluoride ion by ion chromatography, the interference becoming significant at 0.001 mM or higher of metal concentration. The metal interference was suppressed significantly by adjusting the pH of a sample at 12 or higher. The pretreatment of alkalifying samples proved to be very effective for determination of fluoride ion in the presence of metal ions.

2.2 Removal of fluoride ion with active metal oxides and basic carbonates.

Hydrous metal oxides of lanthanum(III), cerium(III), cerium(IV), yttrium(III), titanium(IV), and aluminum(III) were prepared by hydrolysis with ammonia water. Basic metal carbonates of the above metals were prepared by homogeneous precipitation with urea. The adsorption and dissolution characteristics of those materials were studied with fluoride, bromide, iodide, sulfate, phosphate, and nitrate ions. Namely, hydrous cerium(IV) hydroxide and basic cerium(III) carbonates exhibited high selectivity and capacity for adsorption of fluoride ion. The fluoride concentration decreased down to 0.02 mM or lower, showing much higher efficiency than conventional lime precipitation process. Hydrous cerium(IV) oxide has very high dissolution stability, the solubility being inappreciable at pH 2-13. Both fluoride ion and phosphate ion were adsorbed on hydrous lanthanum(III) oxide and basic yttrium(III) carbonate.

41. Catalytic Oxidation of Refractory Organic Substances (1)
(FY 1990-1994)

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Various refractory organic substances such as aromatic chloro and nitro compounds are present at significant concentrations in waste water from organic chemical industries. These chemicals are hardly removed by the activated sludge method and are discharged into the environment where they remain since they are hard to decompose by microorganisms and inhibit microorganism activity. The accumulation of these chemicals in the environment pollutes and destroys the ecosystem. To remove refractory substances in waste water from chemical industries, it is necessary to establish chemical oxidation and biological treatment in conjunction. For this purpose, the oxidative decomposition of refractory chemicals and biodegradability of the reaction products have been studied.

1) Ozonation of nitrophenols

The solutions of *o*- and *p*-nitrophenol, 2,4- and 2,6-dinitrophenol and 2,4,6-trinitrophenol were placed in a reaction vessel (volume:1.5l) and ozonated in the ozone concentration range, 24.7 to 26.0mg/l. Nitrophenols were rapidly reduced and after 30-90min ozonation could no longer be detected. However, TOC was only reduced to about 50% even after 120min ozonation. The degradation of refractory organic compounds by ozonation is thus not complete and subsequent treatment such as application of a biological method is required. Ozonation of nitrophenols led to the formation of oxalic and formic acids as major products and small amounts of malonic and acetic acids. Formic acid increased with ozonation time, reaching maximum after 30-90min, and then decreased. Oxalic acid increased during the reaction, which shows little reactivity toward ozone.

2) Biodegradability of ozonation products

For evaluating the biodegradability of oxidation products, the following method was conducted : To an ozonated solution of nitrophenols is added a non-acclimatized sludge culture. This mixture (MLSS:510- 550mg/l) is incubated for 4days at constant temperature (25°C). At daily intervals, a supernatant is withdrawn and analyzed for TOC. Based on variation in values, biodegradability is evaluated.

Biodegradability of oxidation products of nitrophenols after 0,30,60,90 and 120min ozonation was examined. TOC of nitrophenols was hardly reduced even after 4days incubation, indicating little biodegradability. For the 90min ozonation solution of nitrophenols in which most of them was decomposed, TOC removal more than 80% was attained and TOC in the solution was less than 10ppm. Ozonation thus greatly improves the biodegradability of refractory organic compounds and the result confirms that refractory organic compounds can be treated by chemical oxidation and the biological method in conjunction.

3) Mutagenicity test (the umu-test)

The umu-test is one of the effective methods to detect potential mutagenic activity of chemicals. The principle of the umu-test is based on the ability of the DNA-damaging agents to induce the umu operon. A plasmid pSK1002 carrying a fused gene umuC'-lacZ that produces a hybrid protein with β -galactosidase activity was introduced into *S.tyrimurium* TA1535. Using this strain, TA1535/pSK1002, the umu-test was developed for the screening of environmental mutagens.

The mutagenicity of ozonation products of nitrophenols was examined by this method. 100 μ l of the tester strain culture was poured on the microplate, 10 μ l of the samples of the ozonated solution was applied, then 100 μ l of S-9 Mix for metabolic activation was added. After 2h of incubation at 37°C, β -galactosidase activity produced by the fusion gene was assayed. The effectiveness of this method was previously confirmed by positive effect of 2-aminoanthracene and furylfuramide. For solutions of nitrophenols after 0-120min ozonation, no mutagenic activity was detected.

41. Catalytic Oxidation of Refractory Organic Substances (2)

(FY 1990-1994)

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The waste waters from organic synthesis factories containing aromatic-nitro-compounds or aromatic-chloro-compounds are hard to be treated with usual methods such as a coagulation method or biological technique. This research is aimed at establishing a decomposition method of the refractory organic substances in the waste water with wet oxidation using solid catalysts. As model substances, nitrophenol and chlorophenol were selected and decomposition properties of these substances were studied. Effect of an addition of catalysts such as noble metals supported on carriers or transition metal oxides was tested.

Batch wet oxidation experiments were conducted with a 330ml stirred autoclave. The autoclave was charged with 200ml of 1000mg/l solution of the substances, and pressurized with mixed gas of 80% of nitrogen and 20% of oxygen. Oxygen amount was set to be 1.5 times for a complete stoichiometric oxidation. In the catalytic reaction, 1g of solid catalyst was added into the sample solution. At appropriate times, an aliquot of reacted liquid sample was withdrawn through a cooling pipe, and analyzed.

Wet oxidation of p-nitrophenol without the catalyst was studied at 200°C. The pH value decreased with reaction time, and reached to the order of three. A formation of organic acids was inferred from the result. The value of TOC decreased with the reaction time and removal ratio of TOC became 54% after 150 min at 200°C. Absorption maximums were observed at 225 nm and 317 nm, and absorbances at these maximums were decreased with the reaction time. This result means a decomposition of benzene-ring of phenol. From analysis by high performance liquid chromatography, a decrease of p-nitrophenol peak and an increase of several peaks with

decomposed products were observed. Absorption spectra of the peaks were measured with a photo-diode array detector. Amounts of acetic acid and formic acid were determined by ion chromatography.

Next, Wet oxidation of p-nitrophenol was carried out with catalyst of 5% single noble metal supported on alumina at 150°C. The result was shown in Table 1. Comparing of noble metals, the order of TOC removal was as follows; Pt>>Pd>Rh Ag. With the platinum catalyst, TOC removal became 95% after 150 min at 150°C. And a formation of formic acid and acetic acid was negligible with the catalyst. In the case of catalyst where each 2.5% of two kinds of noble metals was supported on alumina respectively, the value of TOC removal became intermediate between two kinds of 5% catalysts. Alumina, zirconia and titania were compared as supports for 5% platinum catalyst. The highest TOC removal was obtained in the case of titania.

Then, a decomposition of p-chlorophenol was studied. TOC removal was 18% after 150 min at 200°C without catalyst. This TOC removal was small comparing with 58% of phenol. Introduction of chloro-radical into phenol depressed the oxidation reaction because chloro-radical is an electronegative radical. The oxidation reaction was much accelerated with the 5% platinum on alumina, TOC removal became 95% after 150 min at 150°C.

Table 1 Comparison of catalysts for decomposition of p-nitrophenol

| | TOC removal (%) | |
|--------------------------|----------------------|-----------------------|
| | After 30min at 150°C | After 150min at 150°C |
| Non catalyst | 0 | 0 |
| 5 % Ag/alumina | 0 | 6 |
| 5 % Rh/alumina | 0 | 8 |
| 2.5% Rh, 2.5% Pt/alumina | 5 | 13 |
| 5 % Pd/alumina | 12 | 24 |
| 2.5% Pd, 2.5% Pt/alumina | 24 | 78 |
| 5 % Pt/alumina | 31 | 95 |
| 5 % Pt/zirconia | 50 | 93 |
| 5 % Pt/titania | 70 | 93 |

42. Treatment Technology of Waste Water from Waste Paper Recycling
Process
(FY 1990 ~ 1992)

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The recycling process of the waste paper should be further extended for savings of wood resources from the standpoint of global environmental preservation.

To attain the object, there are several problems to be resolved; one is the treatment of the waste water from a variety of papers including high content of inorganic additives such as calcium carbonate and talc, or organic additives such as starch and alkyl ketene dimers for sheet strengthening and sizing, respectively. These organic additives are not easily biodegraded. Furthermore, they interfere with the coagulation of calcium carbonate and talc in waste water treatment process.

This study aims at the development of an effective biological treatment process for the waste water from regeneration processes of waste papers including the above-mentioned organic additives. We planned to search microorganisms which are effective in decomposition of the organic additives. Final object is a development of the economical combination process of coagulation and activated-sludge, wherein the microorganisms are immobilized on oyster or Akoya shells with layered structure.

In this fiscal year, we prepared bioceramics from oyster shells and investigated immobilization of activated sludge on the bioceramics for COD removal. In addition, we examined the effective coagulation method for the waste water from a paper mill regenerating waste paper, and degradability of xylan with the activated sludge.

The results are as follows:

1. Oyster shells autoclaved with water at 140 or 160 °C compared with those at 100 or 180 °C were favorable for COD removal from the waste water with immobilized activated-sludge.
2. An aluminium sulfate coagulant showed lower coagulation ability for the waste water than polymeric aluminium chloride; nonionic poly(acrylamide)

showed higher coagulation ability than anionic poly(acrylamide) with regard to transparency and a TOC removal. In consideration of an economical aspect, a combination of aluminium sulfate and nonionic poly(acrylamide) is promising for treatment of waste water from waste-paper recycling processes.

3. Activated sludge used in this study contained some filamentous fungi which secrete xylanase.

43. An advanced technique for treatments of waste water
containing organic materials
(FY 1991 - 1995)

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Biological waste water from fermentation, food and pulp mills contains large quantities of BOD as decomposed organic materials from cellulose, lignin, starch, saccharide, protein, fatty oil and others. Emulsion oil waste water from machine factories is high emulsified oil and separation of oil and water is very difficult. In this research, we aimed at development of efficient treatment system which decomposed these organic materials in waste water to CO_2 and H_2O .

We have studied on two subjects. First part is measurement of electric oxidation potential of vanillyl alcohol, vanillic acid, vanillylsulfonic acid, vanillin, veratryl alcohol, veratryl aldehyde, veratric acid as model compounds of lignin in pulp waste water. Second part is acid hydrolysis of cellulose as solid matter in biological waste water.

As a result, oxidation potential of model compounds distributed about 0 to 1.2v then these oxidation potentials decrease with increase of pH. The tendency on oxidation potentials of veratryl compounds group more remarkable than in case of vanillyl compounds group.

Hydrolysis of cellulose (sulfuric acid 1%, reaction temperature 190, 200, 210°C) was carried out.

Maximum yields of glucose at 190, 200, 210 °C were 21, 23, 27 %, respectively. On our research aim, total yield of glucose and decomposed compounds(levulinic acid, formic acid and other low molecular compounds) is more important than yield of glucose only. Total yield of these materials was about 50 %.

**44. Behaviors of Synthetic Organic Compounds in Coastal Environment
(FY 1987-1991)**

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This study is designed to investigate the major processes in the fate and behavior of potentially harmful chemicals in coastal environment and to develop a numerical model that predicts the fate of these chemicals. Ise Bay was selected as a model field on whose shore Nagoya, one of the larger cities in Japan, and Yokkaichi which houses large petrochemical complexes are located.

1. Horizontal Distribution of chemicals in Ise Bay Bottom Sediment

The concentrations of Cu and Zn decreased from the head to the entrance of the bay, and from the west to the east coast. There were a good correlation between Cu and Zn concentration, except for the head of the bay.

Concentrations of mono- to hexa-chlorobenzenes in sediment samples of Ise Bay were analyzed. The sites with higher dichloro- and tri-chlorobenzenes concentrations in the middle of the bay covered the area where the sediment particle size was small. This was also the area where downward water flow was estimated to exit. These findings indicated that these congeners were adsorbed by suspended particulate and transported by water flow.

The concentration of TBT was related roughly to ignition loss of the sediment. The area with high concentration of butyltin corresponded to the area with high ignition loss and the simulated downwelling zone. Another area with high butyltin concentration, near Yokkaichi Port, was also located in the downwelling zone. The area near Nagoya Port, which situated in the simulated upwelling zone, had low butyltin concentration. The main transportation process of TBT to sediment is thus the transportation of TBT carried on organic particulate, and this process is affected by not only horizontal surface flow but hydrodynamic down- and upwelling as well.

2. The Behavior of Chlorobenzene

To estimate the transportation mechanism of chlorobenzene from water to sediment, the detailed survey was done at selected sites on water, suspended solid, and sediment in March and August in 1988. The survey indicated that chlorobenzene in the suspended bottom solids and in bottom sediments were not equilibrated with those in the bottom seawater. Based on these results, a hypothetical mechanism which assumes that the chlorobenzene adsorbed by suspended solid at the surface

water layer transport directly with little desorption during the sedimentation was proposed. The behavior of chlorobenzene suggested in this study showed that the use of chemical fate models based on the assumption that the soluble fraction and the fraction adsorbed by suspended particulate are always in equilibrium may yield misleading results.

3. Vertical Distributions of Butyltins and Triphenyltin in the Sediments

Vertical distribution of the concentrations of butyltins, their methylated derivatives and triphenyltin were determined for core sediment samples collected from 4 sites in September 1988 and from 2 sites in August 1991. Triphenyltin and tributyltin concentrations decreased with depth, but the decreasing rate of the latter was less. The vertical distribution pattern of the butyltin congeners showed that the transformation reaction of butyltin depended on sediment conditions and that the methylation reaction was an important process of tributyltin transformation in the deep sediments.

4. Behaviors of Suspended Particulate in Water Column

The size, volume and chlorophyll concentration of the suspended particulate were surveyed along the two crossed lines from the end to the middle of the bay in September 1990.

5. Microbial Activity in the Bay

The anaerobic transformation of trichlorobenzene in sediment, the effect of chlorobenzene on dissimilating nitrate reduction and the activity of sulfate reducing bacteria were studied. Extractable phospholipid fatty acids of benthic sediments collected from Ise bay were analyzed to distinguish the sediment microbial community structure in the bay.

6. Environmental Fate Model of Chemicals

The fate model was developed based on the law of mass conservation and hydrodynamic equation system and include transformation and transport mechanism of chemicals in the coastal bay water, sediment and suspended solid. Reactions included in the model were sorption-desorption and transformation. The simulation was carried out with the conditions which gave good estimation of the distribution of the organic carbon content in the bottom sediment. The simulation result for tributyltin gave the calculated concentration range about the same as the observed range and the simulated higher concentration area was located near the observed high area. The result for 1,3-dichlorobenzene showed the similar distribution pattern in the bottom sediment.

45. Long Range Prediction Model for the Change of Shallow
Water Environment for Optimum Industrial Development(1)
Numerical Modeling for Environmental Change with
Coastal Development in the Tokyo Bay
(FY 1988~1992)

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I. Coastal environment including the geometry and topography is gradually changed over long range with the activity of human being such as reclamation, harbour construction, dam construction, industrial siting and etc. It is necessary to predict such long range change of shallow water region for optimum management of coastal environment. The purpose of this research is to accomplish the assessment model for the effect of such developments over long range change on coastal environment, mainly coastal geometry and topography, incorporated the informations from the various kind of research field such as geology, geochemistry, physical oceanography, marine biology and marine ecology into the model. The field survey from these various aspects is conducted to collect these informations for modelling described as follows : structure of bottom sediment, sedimentation rate, organism succession, pollutant accumulation like heavy metals and organic chemicals among the sediment, historical change of geometry and topography in shallow water region.

1. The cross sectional profiles of water properties has been investigated in the mouth of Tokyo bay at winter. In this result, a clear temperature front was observed at narrow area off Takeoka port.

This front showed features of headland front in response to tidal past offshore Takeoka port. At the both sides of the front, the characteristic quality of biological and chemical properties exhibit. It was expected that the existance in this front is an influence in the distribution of materials in the mouth of Tokyo Bay at winter.

2. Viscous and diffusive sublayers are important to reveal various interaction phenomena between sea water and sediments. But, direct measurement of viscous sublayer in a coastal sea is very difficult. There is only one case. On the contrary, direct measurement of diffusive sublayer is widespread, using oxygen microelectrode.

In this report, a simple evaluation method of both sublayer heights is introduced with the results of three-dimensional current measurement at a reference height above the sea bed. Laboratory formula have many problems in applying the field phenomena. But some orders of both sublayer heights are estimated.

3. The change of bottom topography in the proximity of Huttu Penninsula in Tokyo Bay is simulated by numerical model. The model consists of two submodels ; one is the wave field model and the other is the circulation model. These two submodels are mutually coupled. Firstly, the wave fields in the area for analysis are simulated under the condition which waves come from south resulting from the dominant southerly wind condition. Then the circulation patterns in the shallow water region associated with the wave field are simulated. Using this circulation pattern, a sand transport flues computed and a sedimentation rate is also computed. The results show that the two distinct sedimentation areas appear ; one is the place where shallower bottom stretches out to the south in the southern part of penninsula, the other is the area between the small island (called as DAI-ICHI-KAIHO) and the head of the penninsula. The similated result suggests the area between the island and the head of the penninsula may be connected in future.

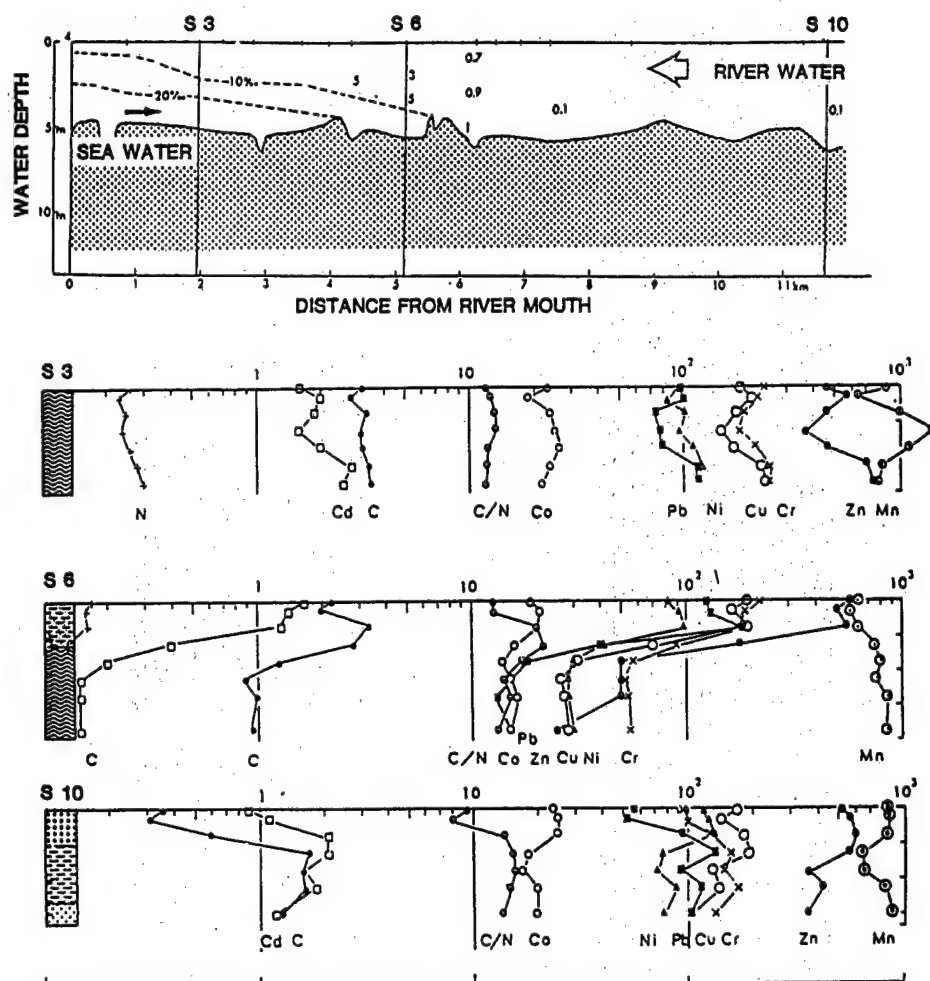
45-II. Long range prediction model for the change of shallow water environment for optimum industrial development
- Sedimentary environment of Tokyo Harbor -
(FY 1988 - 1992)

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Tokyo harbor is situated in the head of Tokyo Bay, which is one of typical estuaries formed by marine flooding in incised valleys in response to Holocene sea-level rise. In an estuary, water is subjected to daily tidal oscillations. There are physical, chemical and biologic processes, which singly or in combination operate on promotion of the deposition and accumulation of suspended sediments.

The circulation pattern of Tokyo Harbor is dominated by river discharges, and tidal effects play a negligible role in the circulation. This study has examined estuarine sedimentary dynamics by historical coastal evolution, particularly detailed analyses of texture, composition, chemical, fabric and biotic communities for surface sediment samples and bore-hole samples through the Holocene, and by direct measurements on sediment and fluid dynamics.

To bring the water quality rating of Tokyo Bay up to Class B, which is suitable for fishing, sewage disposal is required to be able to support marine life. The construction of sewerage plants to perform such a feat would be prohibitively expensive, and moreover the cost of the sewerage would be not only an one-time expenditure but also continuing liability. In other words, though technology can keep death at bay, it alone cannot restore coastal areas of Tokyo Bay to health. Tokyo Harbor, where human activity has produced some of the world's worst environmental destruction, should be an attainable goal anywhere. Restoration projects of Tokyo Harbor must make good use of its natural ability to recover environmental damage. This recovery is accomplished through three mechanisms: sea-water exchange, sedimentation and biological production.



Salt wedge in the Sumida River, Tokyo Bay. Longitudinal profile of the river mouth shows salinity distribution and bottom topography. Vertical variation of content of N, C, Cd, Co, Pb, Ni, Cu, Cr, Zn, and Mn, and C/N ratio. Sampling locations are shown in the profile.

46. Development of New Removal Method of Polluted Sediment in
Coastal Sea

(FY 1988-1992)

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This study aims to understand the behavior of the fresh sediment on the bottom of a semi-closed coastal sea that might arise to develop its removal method in the future, because the fresh sediment often plays important roles in the oxygen deficiency and the eutrophication in the bottom water during summer stratification.

The scientific survey is carried out with respect to the physical and chemical properties such as standing stock, distribution, chemical component, density, the settling velocity kinetics of decomposition of the fresh sediment, etc., and to the fluidity of the fresh sediment corresponding to the tidal change. We choose Osaka Bay of the Seto Inland Sea for study area, which is characterized by very weak tidal current velocity and, eutrophication and oxygen deficient of sea water during summer in the inner part of the bay. The investigation has been completed with respect to distribution, standing stock and decomposition rate of the fresh sediment in the periods of the spring tide and the neap tide, during summer, 1991.

In 1991FY, the results are summarized as follows:

1) Strong bottom turbid layer which may depend on content of bottom suspended particles was not found in the inner part of the Osaka Bay during summer stratification in contrast with the strong and the thick bottom turbid layer during the mixing season of sea water. On the other hand, considerable amount of particulate materials caused by active primary production during summer was observed in the surface water in the inner part of the bay. Although slightly increase in organic carbon

content of bottom particles in the inner part of the bay shows that suspended particulate materials in the surface water are transported to the bottom layer, a large part of the suspended particulate materials in the surface water in the inner part of the bay seems to be transported horizontally to the outside area and to form fresh sediment.

2) Total amount of the fresh sediment (bottom layer suspended particles + bottom particles which may resuspend or move on the bottom surface) could be estimated as 7.6×10^4 tons ($6.3 \times 10^4 + 1.3 \times 10^4$ tons) during the spring tide and 10.3×10^4 tons ($9.1 \times 10^4 + 1.2 \times 10^4$ tons) during the neap tide. This value increased by 2~4 times that of mixing season, as a result of sinking of suspended particulate materials produced by high primary production in the surface water. The fresh sediment during summer corresponded to about 30~40% of total amount of the suspended particulate materials in the whole water volume of Osaka Bay,

3) Decomposition rate constants of organic carbon, nitrogen and particulate phosphorus in the suspended matter collected from the surface and 10 m depths in Osaka Bay were ranged from 0.020 to 0.046 day^{-1} ($t_{1/2}=11 \sim 21$ days), from 0.032 to 0.050 day^{-1} ($t_{1/2}=10 \sim 16$ days) and from 0.030 to 0.066 day^{-1} ($t_{1/2}=8 \sim 17$ days), respectively. While, the decomposition rate constants of those in the fresh sediment collected from the bottom layer in Osaka Bay were ranged from 0.008 to 0.027 day^{-1} ($t_{1/2}=19 \sim 65$ days) for organic carbon, from 0.010 to 0.034 day^{-1} ($t_{1/2}=15 \sim 50$ days) for organic nitrogen, and from 0.023 to 0.043 day^{-1} ($t_{1/2}=12 \sim 22$ days), for particulate phosphorus. The decomposition rate constants of organic carbon and nitrogen, and particulate phosphorus in the fresh sediment tend to decrease with the locations from the inner part to the southern mouth of the bay.

47. Removal Method of Polluted Lake Sediment
(FY 1990 - 1994)

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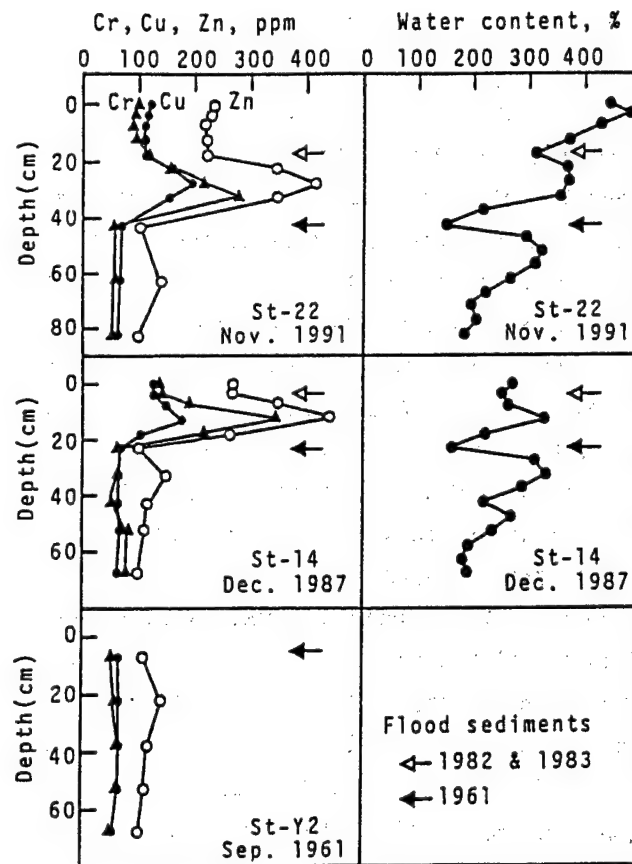
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Bottom sediments in shallow lakes, mean depths of which are less than 10 meters, can be reworked easily by currents and waves caused by wind. In such areas, nutrients are removed from the bottom sediments into the overlying watermass not only by chemical process (dissolution) but also by physical process (reworking). Dredging method for polluted bottom sediments is not necessarily effective to recover good properties of lake water, because dredging of surface sediments also gives rise to outcrop of old heavily polluted sediments and physical mixing between polluted sediments and lake water.

This research aims to clarify the mechanisms of transportation and settling of muddy sediments, and to propose more effective methods to remove polluted sediments in shallow lakes. Studies in Lake Suwa were carried out in F.Y. 1991. High-resolution seismic survey was conducted and 51 core samples were taken. Dredged area is recognizable as depressions about 40 cm

deep in seismic records. Sedimentation rate of mud is estimated to be 10-30 mm per year based on 1) the comparison of vertical profiles of chemical concentration of core samples taken in 1991 with those taken in 1987, 2) on subbottom depths of flood layers in 1961 and 1982-1983, and 3) on topographic changes between in 1965 and 1985. This rate is about ten times greater than in other shallow lakes; lakes Biwa, Kasumigaura, Hamana, Suigetsu and Nojiri. This exclusively high sedimentation rate is attributed to the large drainage area with high reliefs compared with the area of Lake Suwa itself.



Vertical variation of contents of Cr, Cu, Zn in core samples taken in 1961, 1987 and 1991. Arrows show the horizons of flood sediments.

48. Appropriate Flow Control in the Seto Inland Sea by Topographical
Changing Measures for Environmental Enhancement
(FY 1990-1994)

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The diverse and active use of coastal waters is a major subject of further coastal development and requires extensive studies not only to enhance environmental quality but also to expand environmental capacities through active measures for the substance transport on a large scale and long term. Conventional site-by-site environmental assessments pay less attention to active expansions of the environmental capacity and incline more passively to regulations or countermeasures on waste and pollutant discharges from land margins. Therefore we will investigate active flow control to make substance transports appropriate in relevant basins applying topography changing measures. This is because residual circulations are highly susceptible to topography changing and thus responsible for substance transport on a large scale and long term.

Our study consists of hydraulic model studies using the world's largest physical model of the Seto Inland Sea, basic tank-experiments for circulation change mechanisms, and field surveys on actual transport conditions in the areas developed by land reclamation and urbanization. The study progress in FY 1991 is summarized as follows.

(1) Using the physical model, the effects of the largest land reclamation of the Kansai airport in Osaka Bay have been investigated experimentally on long term water-mass transports and circulations in the bay. Models of land reclamation for the middle part of the Seto Inland Sea after 1972 were also installed for such investigations.

(2) Tank experiments with a simple enclosed bay model were carried out to find bay circulation change mechanisms and effective measures to improve the water mass exchange of stagnant water in the bay. The bay bottom slope effects on the bay water circulation were also investigated.

(3) Following the survey in the summer of 1990, a field survey was carried out in February 1992 to investigate seasonal changes of substance transport and water quality in the developed parts of Osaka Bay. Fish damage accidents in the developed area in the past were also examined and have been highly attributed to the intermittent upwelling of bottom sea water with poor oxygen in August and September.

49. Evaluation Method of structures and Purifications
of Shoreline Environments
(FY 1990-1993)

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Shoreline environments are very important for various marine lives and their purifying functions are re-evaluated in today for improving sea water pollution. Some attempts have been made in Tokyo Bay as an artificial seashore. But, we have not so much informations about the purifying functions of sandy beach, tidal flat and artificial seashore. We should accurately reveal them and evaluate these effects on the marine environments.

In this year, the field experiments were made at the tidal flat of Ena Bay, Miura Peninsula in the southern part of Tokyo Bay on September and January.

1. The structure of tidal flat

Tidal flat has not the strict definition. In this report, we adopt the name of tidal flat having following characteristics.

- (1) Slope of intertidal zone is relatively small.
- (2) Soil is almost composed with silt and fine sand.
- (3) Distance of intertidal zone is relatively long.

2. Temperature condition in the tidal flat

Temperature in the tidal flat is one of important factors in that purifying functions. Bottom sediment temperature profiler has been developed for measuring short-period fluctuation of bottom sediment temperature. It is a 60cm length stick with 21 thermistors for measuring bottom sediment temperature. Temperature data are stored in the self-contained CMOS RAM memory recorder.

Vertical profiles of bottom sediment temperature in the tidal flat have been obtained on September, 1991 and January.

1992. Variation of temperature is maximum at one cm from the ground surface and exponentially decreases to 35-cm layer. The ranges of thermal diffusivity in its vertical profiles are $0.31 - 0.45 \times 10^{-6} \text{ m}^2/\text{s}$ on September and $0.18 - 0.36 \times 10^{-6} \text{ m}^2/\text{s}$ on January. These values are similar to ones obtained in the muddy layer.

3. Water quality of inflow and outflow seawater in tidal flat

To clarify the roles of tidal flat for material circulation of coastal seawater, the observations were made at the tidal flat on September, 1991 and January, 1992. The front edge of seawater during the flood tide and the last edge of seawater during the ebb tide were collected at five stations on the tidal flat and the reference seawater was also collected at the entrance of tidal flat respectively in each time.

The concentration of SS (suspended solids) of the reference seawater was relatively low. But, its concentration increased up to 400 mg/l when the front edge of seawater reached to the middle of tidal flat. At the ebb tide, its concentration became under 90mg/l. It is mainly estimated that the inflowing SS deposited on the tidal flat. From comparing another water qualities of front edge seawater with the last edge seawater, Chl-a, DOC and total number of bacteria showed the same behaviors as SS. On the contrary, the concentrations of DO, T-N, $\text{NO}_3\text{-N}$ and DIN were almost same in the front edge seawater and the last edge seawater.

The sulfate reducing activity in the sediment of tidal flat showed low value. The observed ranges of this activity were $0 - 2.3 \text{ nmol SO}_4^{2-}/\text{cm}^3 \text{ d}$ in September and $0 - 6.4 \text{ nmol SO}_4^{2-}/\text{cm}^3 \text{ d}$ in January.

50. Studies on the Anti-fouling Polymeric Materials
(FY 1991-1994)

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Organotin compounds such as triphenyltin are effective for anti-biofouling by releasing from the paint surface to sea water. However, these compounds cause the pollution by depositing in fishes and shells. In this research, the function of interfaces is considered as one of the important causes of adhesion of marine bioorganisms, and the material surfaces which decrease such adhesion are designed and synthesized. Following subject matters were studied.

1) Typical polymeric materials such as polymethylmethacrylate (PMMA), fluorine resin(PTFE), polycarbonate(PC), polyethylene(PE), polyvinylchloride (PVC), silicon resin(Si) and polyamide resin(PA) were subjected to the test of biofouling at Nakaminato, Ibaraki. At the initial stage of fouling, attachment boards were mainly covered with slime. During attached period, attaching organisms were invertebrates such as blue mussel, acorn shells and *Osteridae* and algae. The degree of fouling based on dry organisms weight depend considerably on the surface structure of polymers. The mechanism of biofouling of polymers was also discussed on hydrophobic and dipole interaction basis.

2) Some hydrophilic surface layers has been suggested to be effective for anti-fouling, and therefore the hydrophilic layers were formed by plasma graft polymerization onto polypropylene substrates. The surface was evaluated by contact angle of water using Wilhelmy method. The changes of surface morphology of these grafted layers after dipping in sea water were observed by SEM, and the effects on anti-fouling were compared to that on the untreated substrates.

3) For the purpose of developing the anti-fouling substances, acrylamide copolymers having copper chelate forming group were synthesized. The solubility and phase transition mechanism of these copolymers in water and sea water were studied.

4) Poly(γ -glutamic acid)(PGA) production in *Bacillus subtilis* IF03335 was studied. When citric acid as a carbon source was added to a glutamic acid medium containing L-glutamic acid and ammonium sulfate, a large amount of pure PGA was produced. Moreover, the mode of hydrolysis was investigated with PGA in aqueous solution at 80, 100, and 120 °C by monitoring the time-dependent changes in the molecular weights. In addition, the usage of PGA as anti-biofouling material in sea was studied.

51. Nitrogen Cycling at Sediment-Water Interface in Coastal Marine
Environments
(FY 1991~1994)

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Nitrogen has been recognized as a primary limiting nutrient for eutrophication in semiclosed basin in coastal marine environments. The discharge of nitrogen from terrestrial sources has increased dramatically in recent years, however, and many coastal environments have suffered from accelerated eutrophication. Another significant source of nitrogen for eutrophication is release from the sediment to the overlying water. Organic detritus precipitated onto the sediment is mineralized to inorganic nitrogen through nitrogen cycling at sediment-water interface, and those regenerated inorganic nitrogen recycle into the overlying water. The purpose of this study is to develop a whole ecosystem model including these nitrogen processes quantitatively, which can be highly predictable and may be useful in relation to management practices.

Processes involved in nitrogen cycling at sediment-water interface considering in this study are as follows:

1. Precipitation, sedimentation and resuspension of organic detritus
2. Mineralization of organic nitrogen and ammonium production
3. Nitrification (ammonium oxidation and nitrite oxidation)
4. Dissimilatory nitrate reduction, dissimilatory nitrite reduction and denitrification
5. Pool sizes (concentrations) of nitrogenous compounds in different chemical forms in sediment and in overlying water
6. Adsorption of inorganic nitrogen ions to sediment particles
7. Diffusion of inorganic nitrogen along concentration gradients through sediment-water interface

The main factors regulating the above processes are biological, and the model will be developed with special attention to the role of microorganisms, though there may be great influence of animal activities (biodeposition, bioturbation etc.) on nitrogen cycling.

At the beginning, the seasonal patterns of denitrification activity at sediment surface

were studied at two stations in the most inner part of Tokyo Bay. One station (Stn. B) was shallow, average water depth was around 1 m, and sandy sediment with very high density of benthic organisms. The other station (Stn. E-3) was 10 m water depth and muddy sediment, and the density of benthic organisms was low. The acetylene inhibition technique was used with undisturbed sediment cores. The denitrification activities were always higher at sandy sediment station (Stn. B) than those at muddy sediment station (Stn. E-3). The maximum of activity was observed in the early summer for the sandy sediment, and in the late spring for the muddy sediment. The annual activities of denitrification were $562 \text{ mmol N m}^{-2} \text{ yr}^{-1}$ for the sandy station, and $97 \text{ mmol N m}^{-2} \text{ yr}^{-1}$ for the muddy station.

In order to know the controlling mechanisms of denitrification at those sandy or muddy sediments, which might cause the great differences in activity between two stations, nitrogen cycling at each station were estimated in July, at which denitrification activity was the most active at sandy station, and in November (Fig. 1). There was a high activity in net ammonification at sandy sediment in July and in November, but the activity was very little in both months at muddy sediment. The nitrification activity was very high at sandy station in July, and close coupling of nitrification and denitrification resulted in the highest activity of denitrification through the year. At sandy station, most of oxidized nitrogen (nitrite and nitrate) produced at sediment surface (via nitrification) and/or coming from overlying water was denitrified. This suggests that denitrification activity is higher than the activity of dissimilatory nitrite reduction to ammonia in the process of dissimilatory nitrate reduction at sandy sediment station. The denitrification activity at muddy station was always lower than that at sandy station, and there were good co-relation between the denitrification activity in the sediment and the concentrations of oxidized nitrogen in the overlying water. This suggests that the oxidized nitrogen denitrified at muddy station was mainly coming from the overlying water, and nitrification activity might be very low at this station. At muddy station in November, however, the nitrification activity was very high, and the concentrations of

oxidized nitrogen was actually very high in the surface layer of the sediment. The denitrification activity at the muddy station was still low even in this month, and this might be due to higher activity of dissimilatory nitrite reduction to ammonia. There were many differences in the nitrogen cycling at two stations, and the effects of physical, chemical and biological factors on the cycle and the regulating mechanisms of the cycle should be clarified in the further investigations.

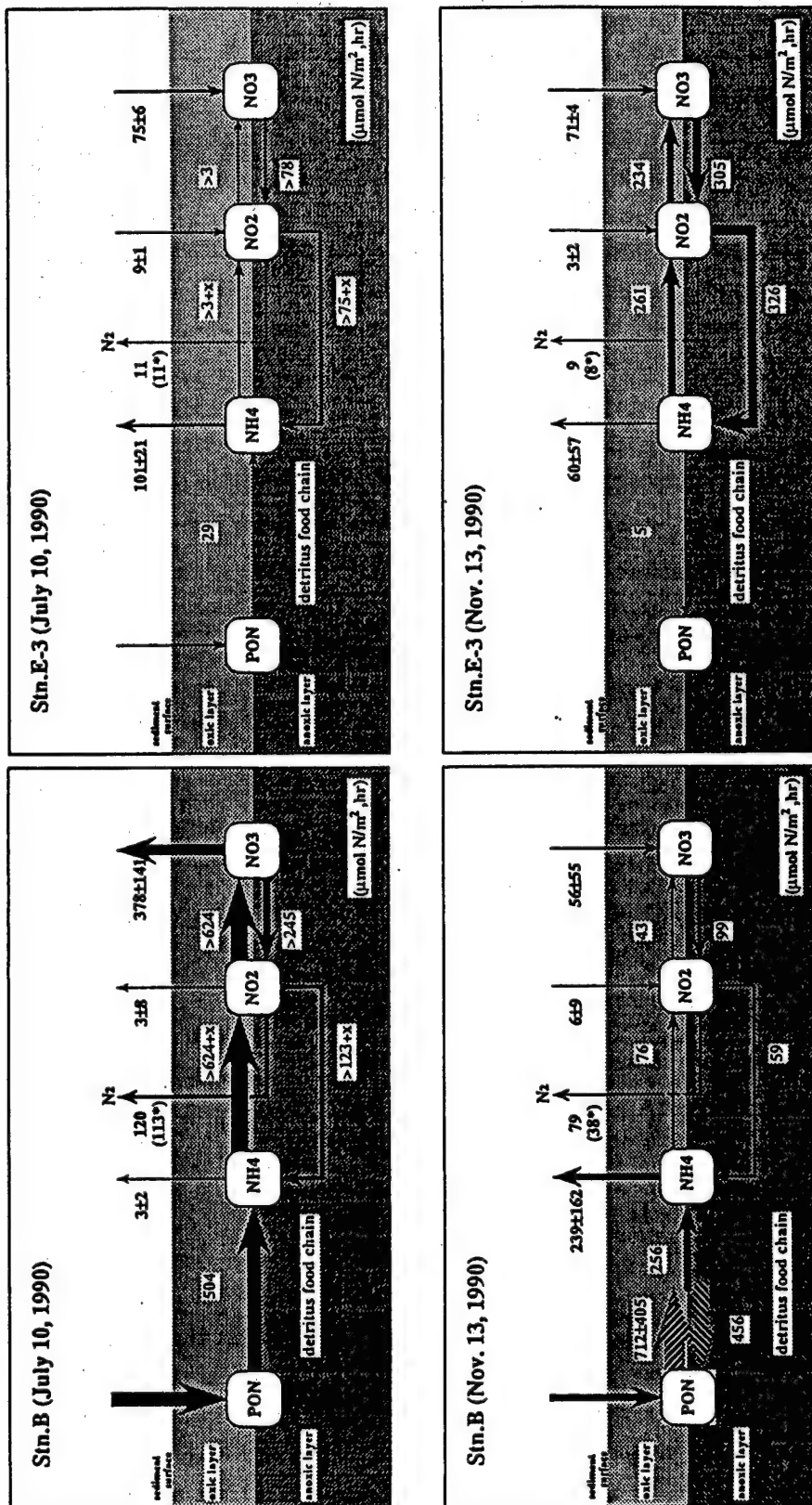


Fig. 1 Nitrogen cycling at sediment surface from 2 stations in the most inner part of Tokyo Bay.
 Stn. B: Sandy sediment with shallow water depth (around 1 m)
 Stn. E-3: Muddy sediment with 10 m water depth
 (DIN fluxes between sediment and overlying water, and dissimilatory nitrate reduction activity and denitrification activity were measured under in situ conditions. Activities of the other processes were estimated assuming steady state conditions.)

52. Treatment of Industrial Wastes Containing Mixed Hazardous
Organic Compounds
(FY1988-1992)

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Hazardous wastes containing halogenated organic compounds should be treated properly to avoid environmental pollution. Incineration is the most feasible treatment for these wastes. However, it is important to clarify the conditions of safe treatment because there is the possibility of forming more toxic compounds during the incineration of some halogenated compounds.

This year, in order to clarify the conditions of safe treatment of certain halogenated compounds, computer simulation of thermal reaction, thermal decomposition experiment using stable isotope compounds and flame mode combustion experiment were performed.

Numerical simulation of $\text{CH}_3\text{Cl} - \text{O}_2$ system was carried out to clarify the decomposition mechanism of halogenated compounds. The effect of temperature was large in $\text{CH}_3\text{Cl} + \text{O}_2$ system and CH_3Cl decomposed rapidly over 1200°C . Reactions $\text{CH}_3\text{Cl} + \text{OH} = \text{CH}_2\text{Cl} + \text{H}_2\text{O}$ and $\text{CH}_3\text{Cl} + \text{Cl} = \text{HCl} + \text{CH}_2\text{Cl}$ dominate at 1100°C .

Reactions $\text{CH}_3\text{Cl} + \text{O} = \text{OH} + \text{CH}_2\text{Cl}$ and $\text{CH}_3\text{Cl} + \text{H} = \text{HCl} + \text{CH}_3$ also decompose CH_3Cl effectively at 1200°C . Addition of H_2 to the $\text{CH}_3\text{Cl} - \text{O}_2$ system caused the change of concentration distribution of OH, CO, CH, Cl and resulted in the change of decomposition rate of CH_3Cl .

The experiment with stable isotope (^{13}C) was carried out to clarify the reaction pathway for the formation of chlorinated benzenes and chlorinated phenols, those are considered to be the precursors of PCDDs/PCDFs. The model waste is the mixture of ^{13}C labeled CHCl_3 and unlabeled $n\text{-C}_6\text{H}_{14}$. A solution of 40wt% $^{13}\text{C}\text{-CHCl}_3$ in $n\text{-C}_6\text{H}_{14}$ was vaporized in N_2 stream and thermally decomposed in a quartz tube reactor heated by an electric furnace. The 2/3 of this reactor from the entrance were pyrolytic (750°C) and air was supplied to the latter 1/3 of the reactor (700°C). Benzene, naphthalene, biphenyls and phenols were formed together with their chlorinated derivatives. ^{13}C contents of all

aromatic products were higher than the that of original mixture. The average number of ^{13}C in each aromatic compound became larger as the number of chlorine atoms in the compounds increased. However, in the case of polychlorophenols, ^{13}C contents were relatively low in some specific isomers(2- and 2,4,6-). This phenomenon is explained that significant parts of these isomers are formed by chlorination of phenol or lower chlorinated phenol while other isomers were formed by oxidation of chlorobenzenes. PCDDs were not detected in this experiment. Mono-through tri-CDFs were detected and their ^{13}C contents were similar to those of PCBs of same level of chlorination. Isomeric patterns of di- and tri-CDFs were compared with those found in MWI fly ash.

Degradability of chlorinated hydrocarbons were tested by flame mode combustion experiment at the composition of $\text{H/Cl}=2$. n-Hexane was added for the compounds those have lower H/Cl than 2. Trichloroethylene, chloroform, carbon tetrachloride and 1,2-dichloroethane decomposed almost completely when flame was stable. However, when the flow rate of air was too high, the flame was lengthened and it became unstable. In such condition, carbon tetrachloride and tetrachloroethylene were emitted as incomplete decomposition products. The upper limit of fuel/air ratio to form stable flame was about 1.7. When fuel/air ratio for trichloroethylene/hexane mixture was 1.82, concentrations of emitted CCl_4 and C_2Cl_4 were 10ppm and 3.7ppm, respectively. Hexachlorobutadiene and hexachlorobenzene were also formed at the order of 0.01ppm. The effect of other conditions such as fuel-rich condition or presence of different hydrocarbon should be evaluated for more variety of halogenated compounds.

53. Treatment and Advanced Utilization of Asbestos Waste
by Transformation of the Fibrous Form
(FY 1990 ~1993)

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Asbestos, which is a naturally occurring inorganic silicates, has been used in many kinds of purposes because of the qualities of heat resistance, tensile strength, resistance to chemical attack. And chrysotile is the most abundant asbestiform mineral in industrial usage. But, it is well known that exposure to airborne fibres of asbestos may results in diseases such as asbestosis, mesothelima and carcinoma of bronchus. Appreciation of health hazards presented by asbestos has resulted in a reduction in the demand for asbestos and an increase in asbestos waste arising. The largest volume of asbestos waste are likely to result from the destruction, alteration and repair of buildings.

Asbestos fibres, particularly chrysotile, are known to be attacked by acids and acid treatment are likely to be capable of achieving a significant reduction in the hazard of chrysotile. The purpose of this research is to investigate the ability of some chemical methods, for example H_2SO_4 acid treatment, heating and acid dissolution and wet grinding, to change the physico-chemical properties of chrysotile, and to develop a new industrial usage of chrysotile in consideration of the removal or reduction of its hazard.

In the second year of the four-year research program, the bending and impact strength of the fibrous amorphous silica prepared by H_2SO_4 leaching of chrysotile was measured to examine a ability as a filler. And, the structural damage (mechanochemical effect) produced by wet grinding in water or HCl solution was investigated by XRD, SEM and IR to convert the chrysotile fibers into fragments.

Further, light scattering phenomena by small fiber was theoretically and experimentally investigated. Scattered light intensity for stratified and unstratified fiber was discussed and measured by varying the refractive index or radius of fiber. A multiwave laser dependent on scattering angle was used as light source. Sample Fiber were made of silica glass and one stratified by polycarbonate. As the results,

experimental results agree with theoretical estimation very well.

The results obtained are summarized as follows.

- (1) Bending strength of the fibrous amorphous silica was comparable to that of commercial glass fiber and potassium titanate fiber. But the impact strength was inferior to that of those materials because of bad dispersion of the silica in plastics.
- (2) By grinding of the silicas in water with ball mill for 2~6 hours, the bundle made up of many fibres was found dispersed into pieces of each fibre. Fibrous form was maintained on this operation, so this silicas seemed to be relatively strong.
- (3) The fibrous form was not varied by grinding of chrysotile and its heated materials under 500°C in water and 0.12N-HCl solution for 24 hours.
- (4) It was possible to convert the fibers into fragments with heating chrysotile above 600°C by grinding in water and HCl solution over 15 hours. In case of water and HCl solution with the concentration of less than 0.12N, the above variation of the form occurred, though dissolution of forsterite and amorphous material in the heated material was scarcely found. On the other hand, the pronounced mechanochemical effect occurred simultaneously with above variation and the dissolution of the components.

54. Research on Waste Treatment of Advanced Technology Products (1)
(FY 1990~1993)

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Recent rapid development of electronic industry facilitates the use of various electronic products in all aspects of our daily lives, resulting in the year-by-year increase in the amount of scrapped electronic products such as obsolete computers. From these waste, only valuable metals of Au, Ag and Cu are being recovered at present; however, small amounts of toxic metals such as As, Sb, Pb and Cr etc. are contained in these wastes. Although no countermeasure is taken to prevent the pollution from these wastes, the rapid increase in the amount of these will be inevitable from now on. Therefore, in order to establish a closed treatment cycle from which no toxic material is discharged, this project consists of fundamental studies on the incineration and the solution purification for the removal of toxic materials and the recovery of valuable metals.

Several potential leaching agents were examined to evaluate the feasibility of a wet process for treating some printed wiring boards(PWB). Leaching agents examined included dilute solutions of hydrochloric acid, sulfuric acid, nitric acid, sodium hydroxide, ammonium hydroxide, ammonium carbonate and ammonium thiocyanate. Leaching with various media was applicable to certain selected items of PWB.

The results obtained in this fiscal year are summarized as follows.

- (1) Cu, Pb, Sn, Zn, Ni and Fe were readily dissolved at 50°C by dilute(0.5 N) HCl to yield metal chloride, but Al was not dissolved so much as well as above metals.
- (2) Results of the leaching of the -200 mesh fraction with 0.5N H₂SO₄ revealed that more than 90% of Cu, Zn and Ni in PWB was extracted at 50°C except for Pb. It was presumed that Pb was transformed to insoluble PbSO₄.
- (3) The incineration of PWB at 400~600°C improved leaching of Ni, Zn and Fe with acidic solution.

(4) Leaching of PWB with HNO_3 showed almost the same results as those with H_2SO_4 or HCl except for Sn. Sn was not detected in the leaching solution because of the conversion to insoluble tin oxide. The extraction percentage of metals in PWB was over 95% under the best condition applied.

(5) The effect of thiocyanate (ammonium salt) was unambiguous because the extractions of Cu, Zn and Ni were enhanced with increasing addition of thiocyanate. More than 1M thiocyanate as well as the addition of Fe^{3+} as oxidizing agent would be necessary for extracting more than 90% of Cu. Au and Ag were not dissolved with thiocyanate salt solution in the absence of oxidizing agents. The extraction of Au was accelerated with the addition of H_2O_2 as oxidizing agent, and the addition of Fe^{3+} was effective for the extraction of Ag.

54. Research on Waste Treatment of Advanced Technology Products (2)
(FY 1990~1993)

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The electronic industry has developed rapidly and one of the representative products is a computer, so that our daily life becomes automatized and comfortable. Consequently, the amount of electronic equipment for disposal is increasing. It contains toxic metals and there is a danger of these metals diffusing to our living space.

To treat of advanced technology products without releasing the toxic metals, this research involves the following mainly using printed wiring board with some circuits (PWBC):

- 1) Combustion treatment to decrease their volume.
- 2) Solution treatment of the gas and residue from combustion process.
- 3) Design and evaluation of combustion process.

As a part of series of the program, the following studies were conducted during the 1991 fiscal year.

- 1) The fate of metals in washed PWBC, in a combustion process, are divided between three streams: residual ash, captured ash and emitted ash. That of pure metals, cadmium, copper, lead and chromium, was experimentally studied using a small-scale experimental apparatus. Metals were found primarily in the residual ash. In some cases, the condensation of the vaporized metals were observed in a part of the experimental apparatus where the temperature was relatively low comparing with another part. This incination was distinguished in the case of cadmium under the atmosphere of nitrogen.
- 2) The fate of PWBC and toxic metals were observed using a batch-type electric furnace. Experiments were performed with the furnace temperature being equal to 400, 600, 700 and 800 °C. The higher the temperature, the faster the completion time of the combustion. The emission rate of NO_x was not affected by the furnace temperature and ranged from 9 to 488ppm. To measure the ratio of weight loss of wasted PWBC in a process of combustion, four kinds of PWBC were used. As a result, the weight of wasted PWBC could

be reduced from 26.6% to 45.5%. These difference comes from the difference of the company, the produced age, the type of machines and so on.

Furthermore, it was clear that the toxic metals were mainly split between the residual ash and the captured ash by the quantitative analysis. Concentration of metals in ash were determined using an inductively coupled plasma atomic emission spectrometer (ICP-AES).

55-I. Microbial Treatment of Natural
Rubber and Plastic Waste
(FY 1991-1995)

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Conventional plastic and rubber materials are causing the serious global environmental problems since the majority of them are non-biodegradable and are not disposed by ecological systems. Recently various kinds of articles using natural rubber and biodegradable plastics are on the market.

In order to establish the microbial treatment processes of rubber and plastic wastes which contained biodegradable materials such as natural rubber and aliphatic polyesters, natural rubber- and polycaprolactone (PCL)-degrading microorganisms were isolated, and effects of some factors on biodegradability of plastics were studied.

Twenty-five strains of Actinomycetes and four strains of Bacteria, which were capable of utilizing natural rubber as sole carbon source, were isolated from soils and deteriorated rubber products. Baiting Method was used to obtain organisms which directly attack solid rubber. Among them, 4 strains degraded more than 30 % of gloves rubber in pure cultures. 9 strains degraded 11 to 26% of the rubber after 4 weeks cultivation period. All the other organisms were also able to degrade natural rubber slowly, though the weight losses were less than 10% in the same period. 2 Actinomycete strains in our culture collection were found to be very strong decomposer of solid rubber. They degraded glove rubber completely within 2 or 3 weeks. One of that two strains degraded the rubber of tyre tread, but at an extremely slow rate.

Some polycaprolactone(PCL)-degrading fungi and bacteria were isolated from PCL-raw cornstarch(CS) blends and PCL-talc blends which were degraded in soil for six months. But their PCL-degrading activities were not strong.

In order to improve the physical properties of PCL and learn what factors aside from chemical structure make conventional plastics non-biodegradable, we studied the biodegradation of blend plastics containing from 10 to 90 wt% PCL by Rhizopus arrhizus lipase. PCL was readily decomposed by the lipase. The biodegradability of PCL changed when it was blended with other kinds of plastics. The blends of PCL and polyethylene (PE) (up to 70 wt% of PE) or polypropylene (PP) (up to 60 wt% of PP) retained high biodegradability of PCL. In the case of the blends of PCL and nylon-6 (NY) or polystyrene (PS) (up to 50 wt% of NY and PS), the biodegradability of PCL did not change so much. In contrast, the susceptibility of blends of PCL and polyethylene terephthalate to hydrolysis by the lipase dropped off markedly.

Effect of phase structure of PCL-PE blend yarns on biodegradability was examined. When PCL was in continuous phase in these PCL-PE blends, these blends disintegrated after biodegradation of PCL. On the other hand, when PCL is in dispersed phase, the PCL-PE blends could not be destroyed even after biodegradation of PCL.

Effect of blend sample miscibility on biodegradability was examined. The miscibilities of the blend samples containing 50 wt% PCL were observed with a scanning electron microscope after removal of the PCL. The PE, PP and NY resin particles were larger than the PS. In general, it seems that the higher the miscibility of the PCL and conventional plastics, the more difficult it is for lipase to degrade the PCL in the blend.

It was found that the weight ratio, phase structure and miscibility of blend plastics containing PCL affected their biodegradabilities.

(FY 1991~1995)

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This research aims to establish a technology for biological degradation of rubber and plastic waste. To achieve this object, the following basic investigations are essential, the clarification of factors affecting the biodegradability, the preparations of standard biodegradable polymers, the development of methods for the evaluation of the biodegradability and their standardization.

In the present study, various biodegradable polymers have been prepared by several chemical approaches. These contain aliphatic polyesters, copolyesters, copolyesterethylenes, copolyesterethers and copolyesteramides. The new polymers were characterized with IR, GPC, DSC, ^1H and ^{13}C NMR spectroscopy.

We have first prepared a new type of aliphatic polyesters, copolyesterethylenes (PEEs), having the mechanical properties similar to a low density polyethylene. PEEs were synthesized by a polycondensation of a higher dicarboxylic acid with poly(ϵ -caprolactone)diols of the molecular weight of 1000, 4000, and 10000. The polymerizations were carried out in the presence of dibutyltin oxide for 6 and 22 hours at 180~195°C with stirring under 1~3 Torr of nitrogen (84~88% yield). The produced polymers have the maximum tensile strength of 20MPa and melt in the range of 50 to 57°C. The molecular weight (M_n) of PEEs was ranged 20000~30000. PEEs are soluble in chloroform and dichloroethane.

The novel copolyesters containing β -methyl- δ -valerolactone (MVL) unit were preliminarily produced. The random copolymers from MVL and L-lactide showed excellent mechanical properties. The properties can be changed from plastic to elastomer, according to the composition ratio of both monomer units. The studies on the copolymerization of MVL with other cyclic esters are now in progress.

A series of copolyesterethers were synthesized by a ring-opening copolymerization of ethylene oxide or propylene oxide with cyclic esters, β -propiolactone, β -butyrolactone, pivalolactone, γ -butyrolactone, glycolide, L-lactide, ϵ -caprolactone and MVL, by using various organometallic compounds as initiators. Copolyesterethers from MVL and ethylene oxide or propylene oxide were newly

synthesized in this study. In general, block copolyethers were produced. However, some selected initiators, which depend on the combination of both monomers, gave random copolymers.

The copolyesteramides were produced by a ring-opening copolymerization of ϵ -caprolactone with ϵ -caprolactam or with α -pyrrolidone in the presence of alkali metal catalysts. The NMR data suggested that the copolymers are constructed by the short blocks of both monomer units. The copolymers were soluble in usual organic solvents. The copolymers of ϵ -caprolactone with ϵ -caprolactam showed molecular weight (M_n) of maximum 20000 and good processability to form into transparent film or sheet.

The films of blends of a copolyesterethylene with biopolyesters, poly(3-hydroxybutyrate) and copoly(3-hydroxybutyrate/3-hydroxyvalerate) were prepared. The blends showed good compatibility in the range of 5~20 wt% of the latter. The mechanical properties were measured for the films prepared by a solution cast method.

The biodegradability for these polymers was evaluated by enzymatic hydrolyses and burial in soil method. Enzymatic hydrolyses were carried out in phosphate buffer solution (pH7.4) at 37°C. The enzymes used were lipases (*Candida cylindracea* and *Rhizopus arrhizus*) and hog liver esterase. The degradation was evaluated by measuring water soluble products using a TOC analyzer. Most of these copolymers were enzymatically degraded. The soil burial tests were carried out for the film (100 μ m) samples in April for two or four weeks. The copolymers were also degraded by microbe in soil. The change of molecular weight and mechanical properties were measured before and after tests.

There are many factors affecting the biodegradability. They are the chemical structure of the main chain, presence of alkyl substituent, the content of ester bond, the melting point, the crystallinity, the random distribution of the constructed units and the hydrophilicity. The biodegradability of copolyesterethylenes was increased with the increase of the ester bond content. The rate of the enzymatic degradation also affected by the shape of the sample, the surface areas.

The effects of above factors on the enzymatic hydrolysis of the copolymers containing aliphatic ester linkage mainly examined on the copolyesterether series. The biodegradability of these polymers was accelerated by the increase with the hydrophilicity and the irregularity in the main chain. On the other hand, this was depressed by the presence of methyl substituent and the high melting point.

These copolymers and blend materials having different degradation duration are considered to be useful as biodegradable standard polymer samples.

55- III. Microbial Treatment of Natural Rubber and Plastic Waste
(FY 1991-1996)

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Rubber and plastic articles are being widely used for various purpose and their total amount has recently shown a marked increase. As the majority of rubber and plastic articles are not decomposed in natural environment, however, a problem of pollution due to their wastes has now been regarded as important with increase in the amount of the articles used. Therefore, development of process for disposal of rubber and plastic wastes is extremely desired now.

The purpose of our study is to establish analytical methods for determining the biodegradability of synthetic polymers and to search the methods to increase the degradability of synthetic polymers.

The results obtained in FY 1991, the first year of the 5 year research program, are summarized as follows:

1. Assessment of methods for determining the biodegradability of synthetic polymers

The modified MITI methods utilizing decomposition by activated sludges and the method testing the degradability by burying the sample film under the ground were useful as the analytical method for determining the biodegradability of synthetic polymers.

2. Factors affecting the biodegradability of synthetic polymers

1) The following trend has been recognized with respect to the degradation rate of poly(3-hydroxybutyric acid) in some soils.

Compost >> Leaf Mold > Copse Soil > Base Manure

2) It is reported that polyglycolide is hydrolyzed nonenzymatically. However, in this study, the modified MITI method showed that polyglycolide was biodegradable.

3) It was found that the blend of polycaprolactone with polyglycolide showed improved biodegradability in comparison with polycaprolactone. Similar improvement was found in the cases of poly(3-hydroxybutyric acid) , and a copolymer of 3-hydroxybutyric acid and 3-hydroxyvaleric acid.

56. Control of Structure-Borne Noise
(FY 1988-1991)

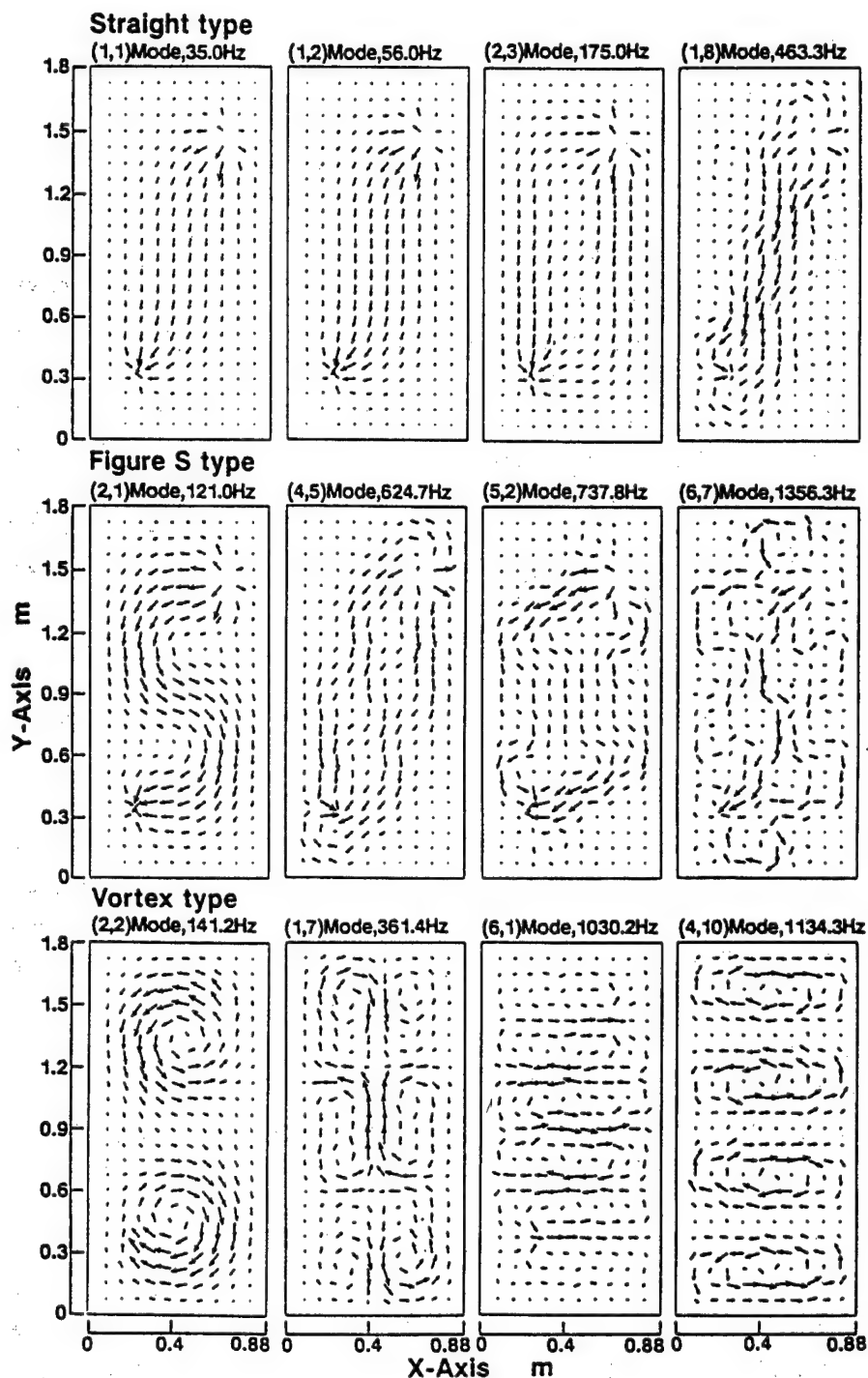
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This report deals with the active control of structure-borne noise radiated from a vibrating plate. It is the purpose of this paper to present a wave control method of a distributed parameter system such a plate. This paper also aims to show the results of visualizing wave propagation. Unlike a conventional modal based control method, this method has the potential of suppressing all the vibration modes of a structure. First, from an analytical point of view, this paper presents three kinds of flow patterns in controlled vibration intensity; that is,

- (1) straight flow patterns from exciting point to control point,
- (2) S shaped flow patterns, and
- (3) rotational flow patterns around the exciting point and control point.

Then, the existence of these patterns are verified experimentally. Next, relationships between vibrational and acoustical intensity are discussed, and also the acoustic power, acoustic pressure in terms of these patterns are clarified. Furthermore, the characteristics of the rotational patterns are clarified, and a mean to generate the vortex of vibration intensity at an arbitrary position of a plate is presented. With a view to applying the active wave control method for suppression of all vibration modes of a distributed parameter system, a new type of moment-driven actuator using a piezo-ceramic stack is presented. Actuators for this purpose are required to be small and light, and still have enough power to control low frequency vibration. So, the fundamental characteristics of the actuators are shown in this paper. Then utilizing the moment actuators, an experiment is carried out to suppress the vibration of a thin plate from the viewpoint of active wave control method, demonstrating three basic patterns of vibration

intensity flow. Finally, the distribution patterns of the acoustic intensity corresponding to each power flow are also shown, the effectiveness for suppressing the structure-borne noise being verified.



57. Psychological and Physiological Measurement
of Fluctuating Low Frequency Noise
(FY 1988 - 1991)

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In order to obtain the basic data to establish the measurement and evaluation method of fluctuating low frequency noise (FLFN) human responses to FLFN were investigated in psychophysical and psychophysiological experiments especially concerned with a typical impulsive FLFN i.e. sonic boom in the present year. And also some measurement and evaluation systems were proposed.

The psychophysical experiments were as follows. At first a stimulus presentation system was constructed to generate impulse waves which were simulated to aircraft sonic booms (N shaped pressure waves). And psychophysical experiments were conducted to obtain subjective ratings of the impulsive FLFN stimuli generated by the above constructed system. In the experiment, the effects of impulsive peak SPL rising time and duration time on human responses were examined. As the results, the obtained ratings increased in accordance with the increment of peak SPL and the duration time from 100 milli-seconds to 120 milli-seconds. And the ratings decreased as the rising time increased.

In an additional experiment, time-constants of human sense were examined by analysis of the continuous ratings of a actual FLFN sample. As the results, it was suggested that the time-constant was about 1.2 second for subjective total intensity and there were great differences in time-constants depending on rating items. For instance about 2 seconds for discomfort and 4.5 seconds for pressure feeling were suggested from the experiment.

A new measurement system was constructed for the total evaluation of FLFN on the basis of the correlation analysis of overall data obtained concerning relationship between human psychological responses and physical properties of FLFN. And the usefulness of the measurement system was examined through its application to actual FLFN samples.

In the physiological study two experiments were performed to objectively

evaluate the effect of fluctuating low frequency noises on the cognitive or emotional process in the central and autonomic nervous systems.

In the first experiment, interference and motivation effects on the cognitive process during the mental works in which subjects had to detect the given serial number were physiologically compared between the actual low frequency noise and natural sound condition. The cortical evoked responses to feedback tones which occurred when subjects detected the given number were measured in all conditions. The result showed that the low frequency noise decreased the working-ratio and amplitudes of evoked responses to feedback sounds. Especially this effect was manifest in the low motivated condition.

In the second experiment, the effect of low frequency noise on emotional states of subjects was examined under the same condition as the first experiment. The frequency fluctuation of alpha wave and variation of heart beat were measured under both low frequency noise and natural sound condition. As a result these measures were highly correlated to emotional states (Fig.1) suggesting the measure were good indices to evaluate the physiological effect of low frequency noise on subject's emotional states (comfort or discomfort).

On the basis of these findings the physiological measurement system for low frequency noise evaluation was constructed.

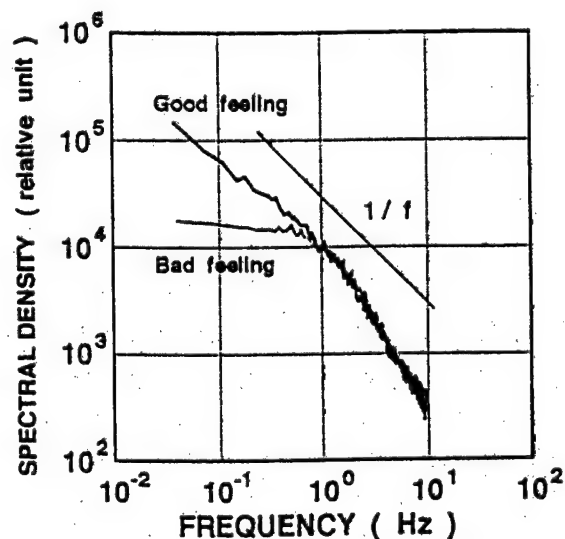


Figure 1. Power spectrum of frequency fluctuation of alpha waves.

58. Outbreak and Propagation Mechanism and Measuring
Method of Impulsive Low Frequency Sound
(FY 1990-1993)

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Sunao Kunitatsu, Atsuko Numao, Hiroyuki Imaizumi,
Tateki Mizuno, Koji Kitabayashi, Susumu Yamamoto,
Hiroshi Yoshikado, Hiroaki Kondo, Norimitsu Shikada,
Makoto Tanaka, Tadashi Suzuki, Michiaki Kinoshita,
and Satsuki Uchida
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By the reason of uniqueness of impulsive low frequency sound for example due to blasting, many measurements and discussion have been conducted since old time, however, there are many unsolved problems concern with such impulsive low frequency sound. Such impulsive low frequency sound is detected sometimes by human body based on some oppression feeling or secondary clattering noise of some structural parts of building. There are many sources of such impulsive low frequency sound in the daily life environment such as blasting operation, traffic impulse against bridge beam, sudden release of high pressure gas and others. In such situation, there is no standardized measuring method, evaluation method and propagation estimation calculation method up to date.

The purposes of the study are to establish following technique based on both field measurements and theoretical discussion;

- (1) Measuring and evaluation method for impulsive low frequency sound
- (2) propagation attenuation estimation method of impulsive low frequency sound
- (3) Response of structural parts of building against impulsive low frequency sound

As the second year of the study, experiments at both laboratory and fields have also been conducted as same as the first year and theoretical discussion have also been carried out concerning with the estimation method for propagation attenuation. Study results are briefly summarized as follows;

(1) For the purpose of physical exact measuring, precise comparison of measured wave form of blast sound by using several types of measuring setup including sound level meters on the market were carried out. The frequency response of each measuring setup have also been examined. Through the discussion, it was found that the measuring setup have to cover the frequency range more than one Hz for the exact measuring of blast sound and due to frequency shift to lower side of blast sound during propagation, measuring error of sound pressure level become larger at measuring points located at longer distance in case the measuring setup only cover the higher frequency range such like more than 20 Hz. Such errors sometimes exceed more than 10 dB at distance around 500m from source. The position of interest of blast sound usually locates at a distance more than several hundred meters away from blasting face, and so, such errors may results in under estimation of the blast sound at the location of interest. In case for measuring at near position to blast sound source, setup with both wide frequency and wide dynamic range have to be prepared.

(2) A new wave form estimation method have been developed for the purpose of attenuation estimation and control of impulsive low frequency sound. As the attenuation during propagation is calculated at each frequency component, the original wave form of impulsive blast sound is transformed to frequency spectrum by the Fourier transformation method. And the frequency spectrum at a receiver after propagation is derived by subtraction remainder from the Fourier spectrum of the original wave and the attenuation value of the same frequency calculated by the acoustical theory. The estimated wave form at a receiver can be derived by the inverse Fourier transformation of the estimated spectrum. Current calculation model of impulsive wave form at a receiver only allow for the effect of ground surface, however, this model will be modified to allow for the effects from meteorological condition. General tendency of the calculated results in both frequency shift to lower side and attenuation shows good agreement with measured results.

(3) From measured results at limestone quarries, distance attenuation of blast sound during propagation, effects of meteorological condition on propagation, directivity index of the bench blasting and others have been discussed. Many measured results show the effects from ground surface, meteorological condition, topography of propagation field, directivity of sound source and others. Some effects of them are able to be explained through the new calculation model mentioned above. The directivity index of blast sound from a bench blasting have been derived through several measurements.

59. Development of Air Monitoring for Individual Components
in Suspended Particles.

(FY 1988-1992)

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Suspended particles in the atmosphere originate in natural and in artificial phenomena such as sea spray, sand storm, diesel exhaust, photochemical reactions and so on. Therefore, the particles contain variety of components. It is necessary to discriminate each components for monitoring the air pollution. In addition the occurrence of these particles and composition of the particles vary with industrial activity and traffic volume as well as weather. This study is aimed to develop a technique to monitor the individual components of the particles and photoacoustic technique was applied for this purpose. This technique will also enable an on-line monitoring of air pollution by suspended particles.

Photoacoustic apparatus, that was main part of the monitoring system, was assembled and the performance was examined in the near infrared region this year. Suspended particles in the laboratory air and soot from paraffin flame was detected with ample S/N ratio by the photoacoustic apparatus using a semiconductor IR laser with a optical fiber output. Figure 1 shows the schematic a schematic diagram of the apparatus. The photoacoustic cell was double tube resonance type with outer (ID=70mm, L=500mm) and inner tubes (ID=15mm, L=400mm). Signal intensities for various air samples are shown in Table 1. Soot concentration was measured by weighing mass increase of filter exposed to the constant volume of the sample air. Estimated sensitivity of the apparatus was about 1.1mV/mg/m^{-3} .

Near infrared absorption spectra of various particle samples and reagents such as kaolin, chrisotile, calcium sulfide, ammonium nitrate and so on were measured with the use of FTIR spectrometer for examining a feasibility of components discrimination by measuring IR spectra of particles. Near infrared photoacoustic spectra of suspended particles of kaolin was measured using the photoacoustic apparatus equipped with an infrared pulse laser system with Nd:YAG, dye and nonliner optics. Suspended kaolin particles were generated by a fluidized bed particle generator. Figure 2a shows the photoacoustic spectra of suspended kaolin particles between 2700 and 2710nm. Absorption peak of kaolin was observed at

2705.5nm, and peaks at about 2701.2nm and 2709.4nm was assigned to absorption band of water. Figure 2b shows the absorption peak of kaolin at 2705.5nm with integration of 256 time. The spectral resolution was about 0.2nm ($=0.28\text{cm}^{-1}$). It may contribute a components discrimination. Absorption bands of kaolin overlapped with that of water in the atmosphere and can not be resolved each other in the spectra measured by the conventional FTIR spectrometer with a resolution of 4cm^{-1} , but those measured with the use of the pulsed IR laser photoacoustic spectrometer can easily resolved each other.

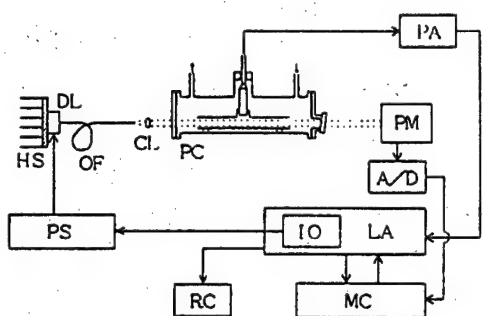


Table 1. PA-signal intensity for various air samples.

| sample | intensity/mV | Soot/mgm ⁻³ |
|---------------|--------------|------------------------|
| soot/air | 12.3 | 9.5 |
| soot/air | 7.2 | 6.7 |
| soot/air | 4.7 | 3.7 |
| soot/air | 2.4 | 2.4 |
| room air | 0.011-13 | - |
| filtered air | 0.007 | - |
| pure nitrogen | 0.001 | - |

Figure 1. The schematic diagram of the photoacoustic apparatus. DL:NIR diode laser(806nm), HS:heat sink, OF:optical fiber, PS:diode power supply, CL:collimator lens, PC:photoacoustic cell, PA:pre-amp., PM:power meter, A/D:analog to digital converter, LA:lockin-amplifier, IO:interface, RC:chart recorder, MC:micro-computer.

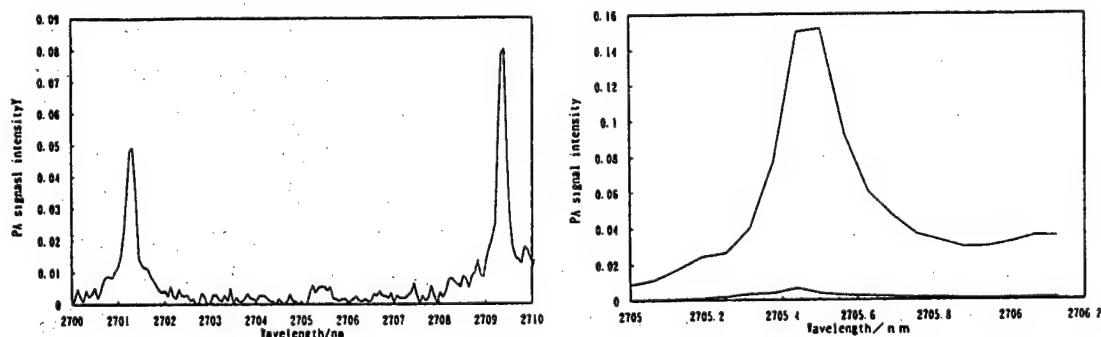


Fig.2. NIR PA-spectra of suspended kaolin by pulsed laser excitation. Integration is 16(left) and 256(right) times for each spectra.

60. Evaluation and Measuring Method of Source Dust
in Consideration of the Relation with SPM
(FY 1988-1991)

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Nobuyuki Kogure, Masaaki Shirahase, (Hideo Ohuchi)
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Since environmental quality standard for suspended particulate matter (SPM) was enacted in 1972, compliance rate with the standard has stayed low level (50-60%) in Japan, and it is a significant administrative problem to improve the compliance rate.

As one of the causes that the compliance rate could not be improved, it is inferred that current public method for measuring source dust can not accurately estimate the actual condition of substances emitted from stationary sources which might change to SPM in the ambient air. The substances emitted from the sources are cooled, condensed or oxidized in the air, and then changed into particles so-called condensed dust.

This research aims to establish the new measuring methods in consideration of the relation with SPM.

In the fiscal year 1991, following investigations and experiments were conducted.

(1) Characteristics of dusts emitted from a stack of experimental combustion furnace fueled with A-heavy oil were investigated by using a flue gas dilution sampling system. The sampling system is designed to measure condensed dusts which generate from condensation of gaseous matters during the process which the flue gas is emitted from the stack into atmosphere and mixed with air. The flue gas in the stack is sucked into the sampling system and mixed with air in a dilution duct.

A large amount of the condensed dusts generated depending on the sampling conditions, and the concentration increased with decrease of the gas temperature and the dilution ratio. Dust concentration measured by the sampling system agreed with one measured by a Type 1 dust sampler in the plume near the exit of the stack, and it was found that the sampling system could measure and estimate the condensed dusts from stationary sources.

Furthermore, the source contribution to SPM was calculated by chemical mass balance method in consideration of the effect of the condensed dust on source data. It was shown that stationary source contribution could increase with increase of the condensed dust because the index elements of source dust were diluted with the condensed dusts.

(2) The inversion method to estimate the size distribution of particles with the extinction spectrum was investigated. A single value decomposition was applied to this inversion method. When Junge and Log-normal types were assumed as the functions of particle size distribution, those distributions were generated from the extinction spectra which were calculated by given size distributions and kernel functions.

As shown in Fig.1, a good inversion solution was obtained, even when the extinction intensity had only effective digit of two. It was found that the accuracy of this method depended on the division numbers in the analysis range of the particle radius and the wave length. The singular value decomposition to the light extinction is useful in size distribution analysis.

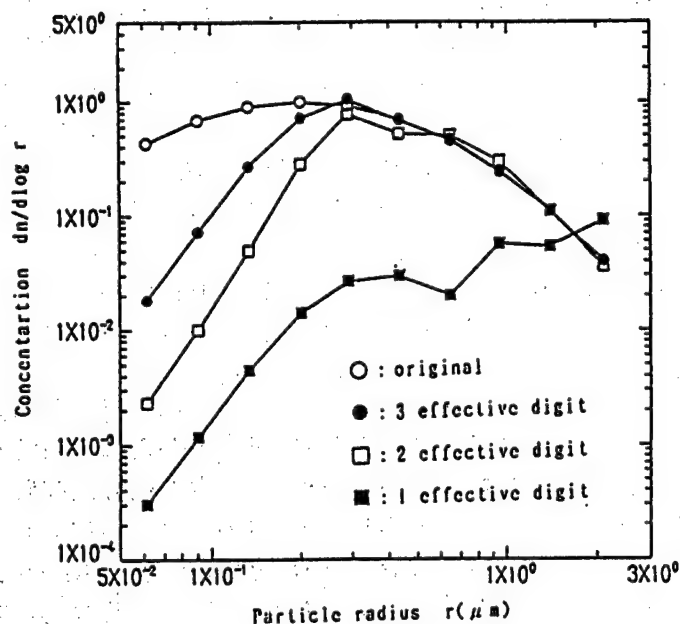


Fig.1 Inversion solutions with difference of effective digits

61-1. Psychological and Physiological Measurements
of Fluctuating Offensive Odors.
(FY 1990-1993)

Neiichi Nagamura, Tsugutake Sadoyama, Sachiko Saito,
Tomoyuki Yoshida and Kokoro Iio.
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Agency of Industrial Science and Technology
Ministry of International Trade and Industry.

The number of reported complaint about offensive odors is the second next to sound-noises among complaints of life-dependent pollution. However, a countermeasure for odor regulations is not sufficient, because the influence of fluctuating odor is not always considered to evaluate offensive odors. Especially, there are few researches about the effect of intensity and time-pattern of fluctuating offensive odors on human. Accordingly, the purpose of this research is to establish the evaluation system for fluctuating offensive odors.

In this year, the degree of unpleasantness to offensive odors was investigated from the point of occurrence-timing pattern of fluctuating odors. First of all, psychological and physiological responses between the intermittent and the lasting pattern of odors were compared. Then, the examined method to measure continuously the physical concentration of a fluctuating odor was examined.

Fluctuating odor was presented to a subject in the odorless small room, using the olfactometer system which was made specially to control the timing (frequency of occurrence and duration of odors) (Fig.1), and the subjective intensity or the degree of unpleasantness was measured in every 10 seconds or continuously. In addition, the final degree of unpleasantness was measured after the finish of exposure of the fluctuating odor.

In the experiment, six kinds of fluctuating odor which were consisted of only triethylamine with different concentration were presented individually to a subject, and the degrees of unpleasantness were compared between the lasting and the intermittent pattern.

As the results, the degree of unpleasantness for the intermittent odor, in which the combination of odor(20 s) and interval air(40 s) was repeated for 10 minutes, was similar to that of the lasting odor, though

the exposing volume of intermittent odor was approximately 20% less than that of the lasting odor.

In addition, the rhythm patterns in both intervals of heart-beat and frequency fluctuation of alpha wave in EEG which were measured simultaneously changed according to the intermittent pattern of fluctuating odor. In the further experiment, the degree of unpleasantness for the intermittent odor was significantly higher than that for the lasting odor under the same exposing volume condition.

These results show that the intermittent pattern is more unpleasant than lasting pattern in the case of triethylamine which is mostly described as the offensive rotten or excretal odor.

On the other hand, the concentration of fluctuating odor applied in the experiments was continuously measured using both the gas sensor-like method and the gas chromatography method which were directory controlled by the valve switch of the olfactometer.

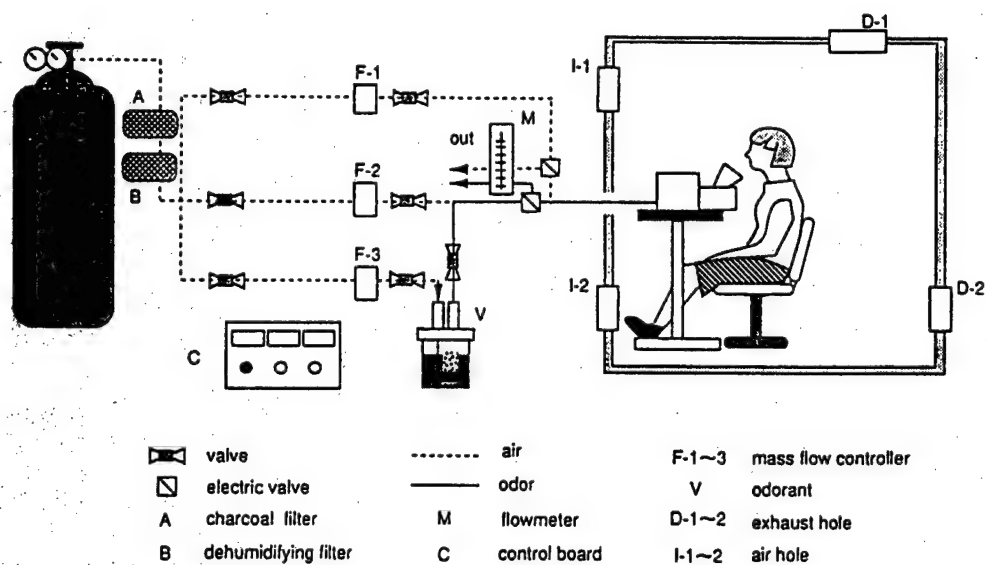


Fig.1 Olfactometer and evaluation system for fluctuating odor stimuli

61-2. Psychological and Physiological Measurements for Fluctuating
Offensive Odors

(FY 1990-1993)

Mitsuo Tonoike, Mari Nakamura, Takashi Hamada and
Masamine Takebayashi

Bioelectronic Interface Section, Life Electronics Research Center

Naoko Kasai, Advanced Metrology Section

Ryuzo Horiuchi, Acoustic Section

Metrology Fundamentals Division

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2. Physiological Measurements and Evaluation of Unpleasantness for
Fluctuating Offensive Odors

Fluctuating offensive odors give us the various psychological and physiological effects and hurt our feeling. Therefore, objective measurements and evaluation of "unpleasantness" for offensive odors are earnestly demanded.

The purpose of this study is to establish psychological and physiological measurements and evaluate a measuring standard for fluctuating odors.

Olfactory evoked potentials(OEPs) and event related potentials(ERPs) have been measured using our odorant pulse-stimulation technique as the objective method for the testing of human olfaction. However, as the olfactory nervous center inner brain is estimated to locate in the deep region, we try to detect the direct responses of these nervous activities from the neuromagnetic field.

A new DC-SQUID sensor system was constructed with high sensitivity, which was designed as a suitable dimension of the pick up coil with 30mm ϕ , 60 mm baseline length to detect the olfactory neuromagnetic field. A new typed magnetically shielded room constructed last year was tested by flux gate magnetometer and a new olfactory stimulator was also used with nonmagnetized materials.

In the present study, the following summaries are obtained.

- 1) We developed the OEP method by using the separation technique with trigeminal responses and olfactory responses.
- 2) ERP method including CNV and the analyses of topographical patterns were also studied to apply the evaluation of unpleasantness of odors.

- 3) We tested the new magnetically shielded room with 5cm thickness of aluminum panels, and obtained the good shielding factor of 50 ~ 100 at 60 Hz and about 270 at 500 Hz frequencies.
- 4) We succeeded to take the sharp odorant pulse with 100 msec duration using a new water-controlled olfactometer. However, sound noise and vibration effects entranced to mix in the experimental data. Now, we are trying to reject these noises.
- 5) New fuzzy technique is applied to evaluate the unpleasantness of offensive odors for our human sensation with the phenomenon of olfactory fatigue.

62. Rapid Determination Techniques of Pollutants
in Groundwater
(FY 1987-1991)

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Groundwater is regarded as one of the precious water resources. However, in recent years it has been found that groundwater is widely polluted by chemical substances. Since groundwater is difficult to clean if it is once polluted, prevention of the pollution is important. Rapid analytical methods for pollutants, therefore, is essential to sufficiently monitor the quality of groundwater.

The object of this investigation is to establish rapid and remote measuring methods for pollutants in groundwater by using laser and optical fiber. This investigation consists of two parts; 1) the development of remote optical fiber fluorometry and chemiluminescence for the determination of organic pollutants such as toxic chlorinated organic compounds, and 2) the development of laser enhanced ionization (LEI) methods for the determination of trace inorganic pollutants.

In this year, following results were obtained.

1) Organic pollutants

For the determination of chloroorganics, the sensor developed in last fiscal year was improved. The sensor is based on the reaction of chlorine gas with luminol followed by chemiluminescence detection. For the oxidizing agents of chloroorganics to chlorine, $\text{HNO}_3 + \text{H}_2\text{SO}_4$ and $\text{NaNO}_3 + \text{H}_2\text{SO}_4$ were tested. The addition of nitric acid or sodium nitrate enhanced the chemiluminescence, and sodium nitrate was more effective for the enhancement. Therefore, $\text{NaNO}_3 + \text{H}_2\text{SO}_4$ was selected as the oxidizing agent. Addition of toxic lead compounds, which was reported in the last year report, was not necessary. Thus the sensor was made more easily and rapidly. The optimum pH of luminol was 8.5, which was the same as the optimum value when $\text{PbO}_2 + \text{Pb}(\text{NO}_3)_2 + \text{H}_2\text{SO}_4$ was used. The optimum concentrations of luminol, H_2O_2 and sodium borate were 0.005, 0.02 and 0.05 M, respectively. Stirring of the groundwater around a gas-permeable mem-

brane was necessary to promote the diffusion of chloroorganics in the groundwater. The stirring led to enhance the chemiluminescence intensity because of the increase of the amount of chloroorganics passing through the membrane. Calibration curve for trichloroethylene with the improved sensor was linear at least from 0.05 to 0.6 mg/l and the relative standard deviation ($n=6$) for 0.5 mg/l was about 3 %. Detection limit was better than 0.03 mg/l. Tetrachloroethylene was also measurable with the sensor although the sensitivity was about 1/4 compared with that for trichloroethylene. These results were obtained using a 1 m optical fiber sensor. A 10 m optical fiber sensor with photoncounting detection also showed the detection limit for trichloroethylene better than 0.03 mg/l. In addition to the luminol method, pyrolysis of chloroorganics by a platinum filament was tested. With this method, calibration curve for trichloroethylene was linear at least from 0.1 to 1 mg/l. However, the sensor with this method was stable around 2 hours in contrast to the sensor with the oxidizing agent (around 15 min.).

2) Inorganic pollutants

Laser enhanced ionization spectrometry (LEIS) at 276.79 nm was investigated for the determination of Tl. At this wavelength, detection limit was 0.043 ng/ml at 200 fold concentration by the solvent extraction with APDC-HMAHMDc/DIBK. The value was about 2.5 times better compared with that at 291.83 nm. Only alkaline and alkali earth elements interfered without the solvent extraction. The effect of laser pulse repetition rate on detection limits and interferences from diverse elements were studied for Mn and Tl. When the repetition rate was increased from 10 Hz to 20 Hz, the detection limits were improved about 20 % and the tolerable concentrations of diverse elements were increased also about 20 %. Mn and Tl in various groundwaters were analyzed by LEIS and compared with the results obtained by ICP-AES and ICP-MS. The results were in good agreement with each other and the applicability of LEIS to real sample analysis were verified.

63. Structure of Lower Trophic Ecosystem in a Eutrophicated Bay - Automated Measurement and
Prediction on Plankton Organisms Succession (I)
(FY 1988 ~ 1992)

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Life Electronics Research Center

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Recently, the progression of eutrophication in coastal bay area has been a social problem. To reveal the mechanism of eutrophication in ecosystem, a great deal of observational and theoretical work has been carried out. However, the plankton organisms succession has not been unknown. Because, temporal fluctuation and spatial variation of plankton species population are quantitatively unknown. An automatic system which analyze of plankton quantitatively at many points is expected. The purpose of this study is to develop this system.

We have developed the basic technique of image analysis for identification of plankton in the preceding years. First, we have accumulated images of typical phytoplankton and zooplankton samples collected in coastal bay area with a conventional microscope and investigated their shape and size with computer. We derived patterns from images and extracted their features for classification from patterns. Then we classified 163 samples to 14 taxonomic groups of plankton using the statistical method and error rate was 21%. To reduce misclassification, we have developed the method using the artificial neural network. Using this method, error rate was decreased to be 10%.

In this year, we have studied precise identification of the plankton and improvement of classification.

For precise identification, pattern recognition of the fine structures of plankton for example legs and feelers is necessary. So far, the features extracted from images simplified structure were used. In thick samples of zooplankton, the in-focus images are overlapped with out-of-focus images, if obtained by conventional microscopy. Therefore we have developed the system that can take in-focus image slices by the laser scanning confocal microscope (Fig. 1). It is able to get the image of extended depth of field in focus from upper side to lower side of the sample by synthesizing the image slices. Binary images were derived from the images of extended depth of field so as to preserve fine structure of plankton. These binary images allow us to extract

features of plankton for their identification. Three-dimensional image can consist of the image slices.

To reduce errors in classification, we investigated the reason of errors which use the neural network. One of the cases that misclassification frequently occur when one sample classified into more than two taxonomic groups simultaneously. Then we used the new neural network algorithm based on the concept of possibility. It classifies samples that have possibility belonging a group into that group. We used the neural network that decides that a sample which belongs to plural groups is "unknown" by threshold detector layer(Fig. 2). We classified 62 samples into 6 taxonomic groups through this network. The error rate was 5% and lower than that with the conventional network.

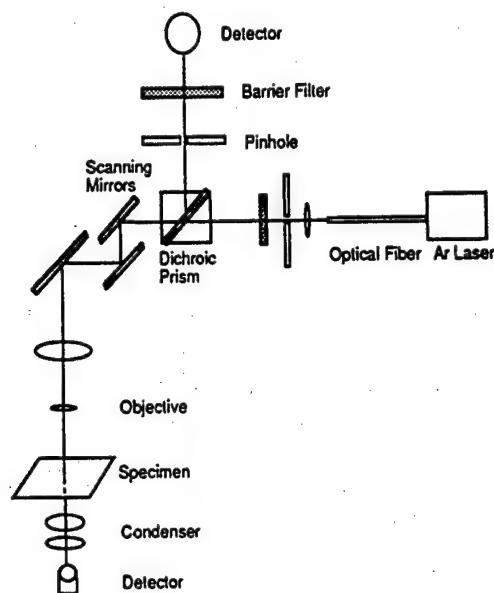


Fig.1 Laser scanning confocal microscope.

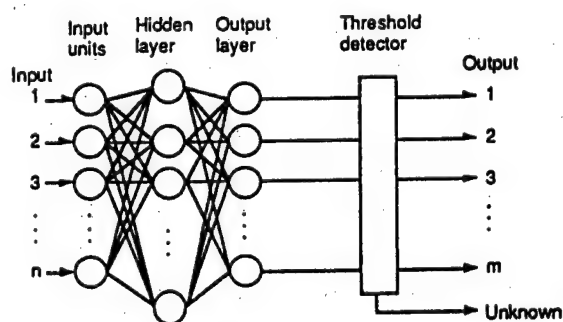


Fig.2 Neural network which can detect threshold value of output.

63. Structure of Lower trophic Ecosystem in a Eutrophicated Bay -
Automated Measurement and Prediction on Plankton Organisms
Succession (II)
(FY 1988 - 1992)

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and Fumio Horiguchi

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In order to develop a model for phytoplankton species succession in a coastal area, a general, size- based simulation model is considered to investigate the dynamics of carbon and nitrogen flow in plankton communities. In the model, community structure and processes are all size-dependent, and all model parameters are determined by body size, using empirically determined relationships calculated from published data. Major flows include carbon fixation, extracellular release of produced dissolved organic carbon (PDOC), nitrogen uptake, respiration, grazing and sinking, etc..

The model plankton community consists of autotroph and heterotroph continua (which are divided into a number of size classes; size spectra), a detrital pool and dissolved nutrient pool. The model aims at the simulation for the size spectral change in response to an environmental stress or trophic interaction. In this year, model program has just developed and tested using some examples. Model calibration and verification will be conducted in the next fiscal year.

64. Study on Techniques of Predicting Environmental-related
Parameters for Advance Environmental Assessment of
Chemical Substances
(FY 1990 ~ 1993)

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Prediction of environmental-related parameters: Advance environmental
assessment of chemical substances.

Studies were carried out for predicting decomposition properties of
chemical substances from their chemical structures in atmospheric, aquatic
and soil environments.

1. Prediction of decomposition properties of chemical substances in
atmospheric environments

Strictly speaking, various factors should be taken into consideration,
when molecules decompose in the atmosphere. Molecules are decomposed not
only by light such as visible radiation and ultraviolet ray, but also by
reaction with chemical species existing in the atmosphere and especially in
the stratosphere. In this study, we decided to predict the general
decomposability and decomposition pattern of chemical substances without
restricting the origin of decomposition.

The "bond dissociation energy" was introduced as an index to
decomposability. The bond dissociation energy of a substance A-B is defined
as the heat of formation of the following dissociation reaction



where A and B represent the product atoms or radicals and g indicates gas
phase. The semiempirical molecular orbital method was applied to calculate
the heat of formation, since it costs short calculation time and it has
comparatively high reliability.

We started with hydrocarbons, halogenated hydrocarbons, ketones, and
ethers from the following points of view.

- (1) It is well known that atomic parameters for such light atoms as carbon,
hydrogen, nitrogen and oxygen are comparatively reliable.
- (2) A lot of experimental data are accumulated for such fundamental organic

compounds.

(3) Chlorofluorocarbons (CFC) have attracted much attention recently, because they cause the destruction of ozone layer and most of the alternatives to CFC are also halogenated hydrocarbons.

For more than thirty chemical substances, the bond dissociation energy is calculated by two typical semiempirical molecular orbital methods, MNDO and PM3. It has turned out that the correlation between experimental and calculated bond dissociation energy is fairly good for both methods as shown in Fig. 1. We are planning to extend calculation to other types of substances including inorganic molecules.

2. prediction of decomposition properties of chemical substances in aquatic environments

Chemical substances in aquatic environments are considered to be decomposed by various factors such as water itself, light, metal ion and existing chemical species. It is not easy to predict decomposition properties of chemical substances, due to these various factors. Therefore, in this study, in order to make the approach possible, we limited to estimate the decomposition properties of chemical substances, only due to water itself, that is, to predict the hydrolysis properties. In order to predict the hydrolysis properties of chemical substances from their chemical structures, it may be possible to collect as many experimental data on the hydrolysis properties of chemical substances as possible and to analyse those data by using parameters related to chemical structures.

For that purpose, references on the hydrolysis properties of chemical substances were collected, from which reliable experimental data on the hydrolysis rates for 157 kinds of chemical substances were collected. Those experimental data on the hydrolysis rates of chemical substances can be classified into 12 chemical groups. Among those chemical groups, we decided to study on predicting the hydrolysis rate of carbamates from their chemical structures. The reason is that there are 18 carbamate compounds the experimental data on the hydrolysis rate of which are collected, those hydrolysis rates ranges from 10^{-2} to 10^{-14} per second, and that some of carbamate compounds are main components of agricultural chemicals. The structure of carbamate compound is shown as $R_1R_2N-C(=O)-OR_3$, and the carbamate compounds whose experimental data on the hydrolysis rate are collected are the combination of molecules with various substituents R_1 , R_2 and R_3 . Therefore, the experimental data of the hydrolysis rates of 18 carbamate compounds were analysed with the multi-regression, where the

electronic parameter σ I were selected as the substituent parameters. For the substituent without σ I, it was estimated from the correlation between σ I and the electron density calculated from the semiempirical molecular orbital method. As a result of the analysis, it was found that the experimental data of the hydrolysis rates of the 18 carbamate compounds can be explained in the accuracy of about 2 order of magnitude. Since the accuracy of this explanation is not considered to be satisfactorily high, we studied to estimate the hydrolysis rate with higher accuracy.

3. Prediction of decomposition properties of chemical substances in soil environments

The soil is the most complicated environment because there are many factors affecting the decomposition properties of chemical substances in the soil environment. Therefore we have to take some model to analyse and estimate the decomposition properties of chemical substances in the soil environment. In this study, we analysed the experimental data on the decomposition properties of chemical substances in the soil environment, only by considering the remaining properties of chemical substances. In order to take the same procedure as that of the hydrolysis mentioned above, the references on the experimental data of the remaining properties of chemical substances in the soil environment were collected. Among those data, the experimental data on the remaining properties of agricultural chemicals were analysed in this study with the same procedure as above.

65. Study on the Reductive Degradation of Harmful Organic Compounds.

(FY 1991-1995)

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The objective of this investigation was to develop the process to treat organochlorine compounds in water.

The first phase of experiments was designed to investigate the effect of reaction condition on the reduction of tetrachloroethane with metallic iron by batch reactor. The second phase of experiments was to investigate the reduction of trichloroethylene with reduced iron by continuous flow system. The model compounds chosen for this work were trichloroethylene and tetrachloroethane.

1. Reduction of tetrachloroethane in the presence of reduced iron

The reductive degradation with Iron powder was conducted in an aqueous solution of tetrachloroethane. The starting concentration of tetrachloroethane was 10mg/L, and the reaction conditions for all studies were as follows: pH 5.5-10.5, 5-40°C and reaction times up to 240 min. The concentration of tetrachloroethane and degradation products were followed over time. In the course of reaction, gaseous products were evolved, and these were later identified as hydrocarbon, hydrogen gas and a extremely small amount of parent organochlorine compound.

The chemical reduction was affected by the temperature, but even if at 5°C degradation was occurred. It was observed that the reaction rate increased with increasing temperature. But according to our experiments, this was lead to the larger volume of hydrogen evolution. The most effective results were obtained when oxygen was previously removed. Perhaps by the presence of oxygen, the surface of reducing agent was partially oxidized and then the reducing ability of metal iron was quickly lost. All the oxygen need to be removed from the influent.

In the presence of electrolytes reduction rates were varied by the species of anion. some electrolyte retarded the reaction rate but some enhanced. The reaction rates were decreased when the concentration of NO_3^- ion was over 20mg/L. But these higher concentration of NO_3^- was not found in ordinary waste water. Redox potential was decreased less than -

300mV before reaction began to occur. The reductive destruction was best accomplished by using an adequate amount of the reductant and contact time up to 120 minutes at ambient (5-30°C) temperature.

2. Reduction of trichloroethylene by packed column

The reductive degradation with metal iron was tested to degrade trichloroethylene by the flow reactor. The concentration of trichloroethylene in the influent was about $100\mu\text{g/L}$. The reactor used here was packed column flowing upward and the size of reactor was 11mm i.d. and 250mm h. with jacket.

In the batch reactor, The reduction rate was affected by the co-existing anions. But in the flow system, almost the same reduction rates were obtained irrespective of ion species. The reduction column operated most satisfactorily at a pH near 7; too low a pH results in excess reductant consumption. Too high a pH lead to deposition of Fe(OH)_2 on the reductant surface, and resulted in shorter life of reductant.

The percentage of the disappearance of trichloroethylene was one of the indicators for the reduction rate but it didn't show whether all the chlorine was extracted from the carbon skeleton or not. We analyzed the concentration of chlorine in the effluents. When enough contact time was given, complete or nearly complete degradation was obtained, and analysis of waters showed that the bulk of the chlorine was removed from the parent compound even if at below 10°C.

The main component of evolved gas phase was hydrogen, which may be due to the decomposition of water. The major reduction product of trichloroethylene was the chlorine-free hydrocarbon: ethylene, and the other components were ethane and acetylene. The composition of these products was varied widely by the reaction conditions i.e. concentration of trichloroethylene, flow rate, reaction temperature and residence time. The formation of ethane was shown to increase with increasing temperature or with increasing residence time. Acetylene was only observed in significant quantities when the concentration of trichloroethylene was above 300mg/L.

66. Efficiency Improvement Techniques for Evaluation Methods
on Exhaust Emission Control System
(FY 1988 ~1992)

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Institute, Ministry of Transport

In an effort to minimize the problems on vehicle pollutions, emission rates from new vehicles have been limited by the tightened regulation standards since over a decade ago. However, even a most advanced vehicle, which has a computer controlled engine and a three-way catalytic converter, possesses also possibility to cause high emissions due to abnormal operations in emission control system. Therefore, the inspection and maintenance techniques applicable to in-use vehicles are required.

The objective of this study is to obtain possible and effective technical methods to keep lower emission levels of vehicles throughout their lifetimes. The approaches to them have been carried out by following strategies:

- (A) The procedure for short emission test to inspect in-use vehicles was considered. The test is aimed at identifying the vehicles with high emissions caused by faults in emission control system.
- (B) The advanced onboard diagnosis (OBD) methods for emission control system were discussed. The OBD should be designed to check the function of engine air-fuel control and the performance of three-way catalyst. If abnormal states relating to high emissions are detected, the OBD may inform the driver of it to take appropriate actions to repair the malfunction.
- (C) For the assistance of works in service shops to make a quick and proper diagnosis of malfunctions occurring in in-use vehicles, a diagnostic expert system that can operate on a personal computer should be constructed.

As to the short inspection test mentioned above (A), following points were clarified.

- ① The emission test procedure is as follows; the test vehicle is driven to trace M4 mode pattern on the simple type chassis dynamometer (S-CHDY) which generates electrical inertia force as a load, and the tailpipe CO, HC and NO concentrations should be measured simultaneously to evaluate those mean values.
- ② The necessity of NO₂ measurement as to evaluation of NO_x emission has been discussed here. As results of experiments with/without the converter device that can changes NO₂ in sample gas to NO, it was found that a normal vehicle emits little NO₂, on the other hand, when air-fuel ratio is deviated to lean side due to abnormal operations, NO_x in exhaust gas contains NO₂ with a rate of

approximately 10 to 20 % in it. However, in such a situation, increase in NO was so remarkable, that it may be unnecessary to measure NO₂ in the emission test for identifying abnormal vehicles.

③ Experiments showed that simply averaged values for CO, HC and NO concentration during the test period do not have sufficient correlation to each component's mass values. To solve this problem, the authors developed a new calculating method to evaluate mean concentrations weighted with each mode's exhaust gas volume.

④ In this method, however, new problem arises. When the tailpipe gas concentrations are continuously measured by a low response analyzer, modal separation for gas concentration in M4 mode is apt to be obscure. The compensative calculating method to improve its response was then discussed.

For the second subject mentioned above (B), the OBD method to monitor the function of air-fuel ratio control system and the performance of catalytic converter reaction was considered. To detect abnormal states concerning with high emissions, a dual oxygen sensor (using pre- and post- catalyst oxygen sensors) method was introduced. To examine the feasibility of this method, on road experiments were conducted using the test vehicle equipped with three-way catalyst system.

In this method, the OBD system works as following way: By monitoring the signal oscillatory states from a pre-catalyst oxygen sensor, engine air-fuel ratio condition can be checked whether it is stabilized near stoichiometric point or not. By comparing the signal from the pre-catalyst oxygen sensor to that from a post-catalyst sensor, the adsorption and reaction performance of a three way catalyst can be identified.

For the third subject mentioned above (C), we developed a programme for the prototype diagnostic expert system that assists the works to search the malfunctions relating high emissions. The knowledge base in this system involves diagnostic rules and net-work framing procedure to select malfunction area in emission control system. The large amount of information for vehicle structure is accumulated on the external data-base, and the expert system can draw and use the necessary data in it for execution of diagnosis. To verify effectiveness of this diagnosis, imaginary defects in an EGR control system were set up and diagnostic simulation was made on that expert system.

67. New Technologies to Control NOx Emission from Diesel Engines and
their Applicability under Actual Driving Conditions
(FY 1990 ~1994)

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Traffic Safety and Nuisance Research Institute
Ministry of Transport

The objective of this study is to clarify basic concepts of NOx reduction techniques from diesel engines and to search technical possibilities for drastic NOx reduction under actual driving conditions.

For above purposes, experimental studies on NOx reduction methods in the combustion chamber are planned to be held with a single cylinder research engine by modifying combustion control elements concerning the fuel injection system, the intake system and the combustion chamber.

On the other hand, NOx reduction effect and emission behavior of other exhaust components under actual driving conditions by various NOx control techniques will be experimentally studied with commercial automotive heavy-duty engines. Possibilities of after-treatment of NOx at exhaust system is going to be studied also.

In this fiscal year, the following studies were carried out. For the study on low NOx combustion method, effect of water emulsified fuel on NOx and smoke emissions was experimentally analyzed by supplying water emulsified fuel with a specially prepared water fuel mixing device at the inlet of fuel injection pump.

As results, it is clarified that NOx and smoke can be deducted simultaneously with the use of water emulsified fuel. This NOx and smoke reduction effects are not affected by EGR and thereby, effective NOx reduction can be possible with the use of emulsified fuel under EGR conditions because of the additional NOx reduction effect by EGR besides that of emulsified fuel.

On the other hand, the increase in smoke with the use of EGR can be suppressed with this fuel. So the trade-off between NOx and smoke emissions can be improved drastically with the combined use of EGR and emulsified fuel as shown in Fig.1.

To analyze the effect on simultaneous reduction of NOx and smoke emissions, the combustion behavior was experimentally investigated with the measurement and the data processing of the cylinder pressure. According to the combustion analysis, the reason of smoke reduction can be explained by the enhancement of diffusion combustion period and shortened total combustion duration time.

Then, for realizing this kind of combustion, a high pressure in cylinder air injection method which aims at enhancing the diffusion combustion was considered and the experiment for trial was carried out. And then, the possibility was recognized for this kind

of combustion control with in-cylinder high pressure air injection at the diffusion combustion period.

In the next year, more detailed investigation will be carried out for clarifying the influences of air injection timing, engine operating conditions etc. The possibility of simultaneous reduction of NOx and smoke with the combined use of this method and EGR will be studied also.

On the other hand, exhaust gas mass emission behaviors under various engine test mode operations such as Japanese diesel 13 mode, diesel 6 mode, EC 13 mode, U.S. heavy-duty transient test cycle(1199 mode) and M15 mode, which is modified test cycle from Japanese 10 mode, were experimentally compared for analyzing the difference of EGR effect on NOx reduction and emission characteristics of other components. The EGR system used this experiment was available to control EGR rate depending on the engine load and speed.

As results, in the view of NOx mass emission characteristics, new Japanese diesel 13 mode test cycle is almost equivalent to U.S. 1199 mode and M15 mode test cycle. Thereby, it seems to be reasonable to use diesel 13mode for the evaluation of NOx reduction techniques. A combined system of EGR and a methanol fumigation, which was experimentally studied under steady-state conditions last year, was applied for this test mode operation and the effect on exhaust mass emissions were experimentally studied. Then, it was found out that one half of NOx reduction could be possible without increase in particulate emissions with this method by controlling EGR rate and methanol mixing ratio properly according to the engine load as shown in Fig.2.

In the next year, several engine test modes will be constructed for trial based on actual vehicle driving patterns on the road, and then, to clarify engine operating regions and NOx reduction level which should be covered by the new NOx reduction techniques, a series of experimental analysis will be carried out under those test modes. Then, according to these results, the representative method for evaluating NOx reduction techniques will be considered.

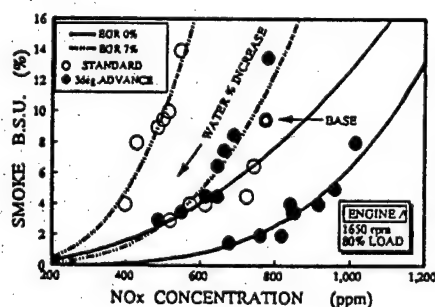


Fig.1 NOx and Smoke Reduction Effects by Water Emulsified Fuel

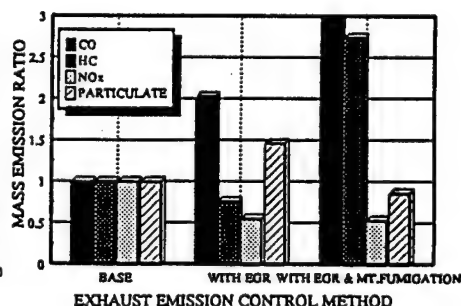


Fig.2 Comparison of Exhaust Emissions under 13 Mode Test

68. Study on Reduction of Exhaust Gas Emissions from Marine Diesel Engines

(FY 1991-1994)

**Keijiro Shiode, Yasuo Miyagi and Kazumi Nishikawa
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Abstract

The engine performance and emission characteristics of a high speed adiabatic diesel engine operated on water emulsified fuel were experimentally investigated. The experiments were carried out by using two types of diesel engines: a conventional metal diesel engine and an in-cylinder insulated diesel engine. Water emulsified fuels containing water of up to 50 vol.% were evaluated by the two types of diesel engines.

Higher temperature of working gas and higher surface temperature of combustion chamber walls were obtained by the diesel engine with in-cylinder insulated combustion chambers.

ENGINES USED FOR EXPERIMENTS

A small, high speed, air cooled, 4 stroke cycle diesel engine was used for the experiments as a base engine and its principal particulars are shown in Table 1. This base engine (a conventional metal diesel engine) was partly modified in order to insulate thermally combustion chamber walls. Ceramic materials such as silicon nitride and zirconia were used for insulating the combustion chamber walls. Ceramified components are shown by the shadowed portions in Fig.1. Combustion space is surrounded by ceramified components when a piston is around top dead center.

PROCEDURES AND RESULTS OF EXPERIMENT

INSULATING EFFECT

The effect of insulating the combustion chamber walls on working gas temperature was investigated by the experiment. Typical examples of gas temperature differences between the conventional engine and the insulated diesel engine are shown in Fig.2.

EFFECT OF WATER ON COMBUSTION

By increasing water concentration of water emulsion fuel, water emulsion fuel reduces not only its cetane number, but it increases also fuel quantity injected, its viscosity, latent heat of evaporation and air entrainment.

These changes give much influence on fuel-air mixing and combustion. Effect of water concentration of emulsion fuel on combustion duration were investigated by the experiments. Effect of water concentration of water emulsion fuel on ignition timing and combustion duration is shown in Fig.3. Since the beginning of combustion retarded and the end of combustion advanced with an increase of water concentration of water emulsion fuel, consequently the combustion duration was significantly shortened. In the case of 50% water emulsion fuel and an insulated diesel engine, the beginning of combustion was retarded by about 4 degrees in crank angle, but the combustion duration was shortened to about 67%, compared with that of gas oil.

EFFECT OF WATER CONCENTRATION ON EMISSION CHARACTERISTICS

Water concentration of emulsion fuel affected not only combustion characteristics remarkably, but also exhaust emissions.

Examples of effect of water concentration on NO_x, CO, smoke emission rates and specific fuel consumption rate, when water concentration in emulsion fuel was changed from 0 to 50 vol.%, are shown in Figs.4-6.

CONCLUDING REMARKS

The followings are found:

Combustion at higher operating temperatures results in significant changes in diesel combustion and emission characteristics, compared with a conventional diesel engine. NO_x and smoke emission are greatly and simultaneously reduced without increasing specific fuel consumption rate by the use of water emulsified fuel and an insulated combustion chamber. But CO and THC emissions increases at high water concentrations. So it is necessary to improve CO and THC emissions at high water concentrations.

Table 1 Principal Particulars of Test Engine

| | |
|----------------------------|--------------------------------------|
| Manufacturer | Mitsui Deutz Diesel Engine Co., Ltd. |
| Model | F 2 L 9 1 2 |
| Cycle | 4 |
| Type of combustion chamber | Direct |
| Air intaking method | Naturally aspirated |
| Cooling method | Forced air cooling |
| No. of cylinders | 2 |
| Cylinder bore | 100 mm |
| Stroke | 120 mm |
| Rotational speed max. | 2,300 rpm |
| Displacement | 1,885 cc |
| Compression ratio | 17 |
| Mean effective pressure | 6.37 bar |
| Max. continuous rating | 23 kW (31 PS/2,300 rpm) |

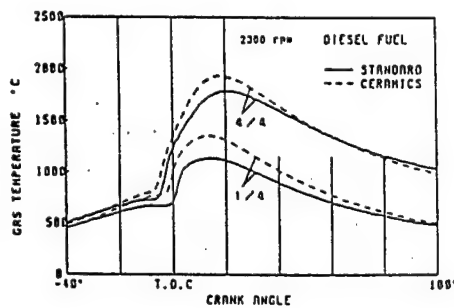


Fig. 2 Gas Temperature Difference between Metal Engine and Ceramified Engine

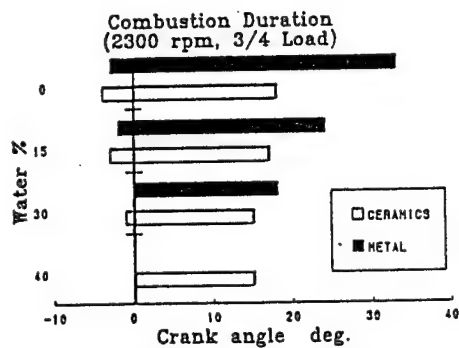


Fig. 3 Comparison of Combustion Duration

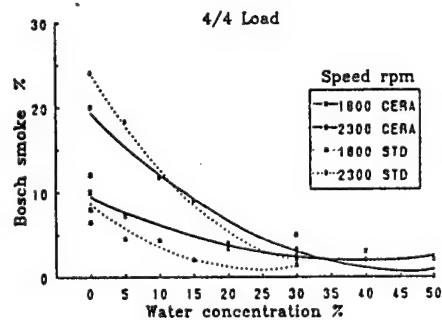
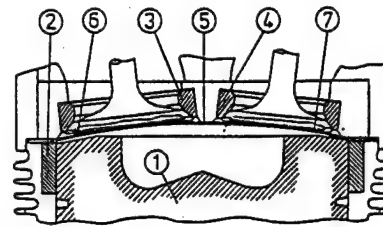


Fig. 5 Effect of Water Concentration on Smoke Emission



Silicon-nitride

① Piston

Partially Stabilized Zirconia (PSZ)

② Cylinder sleeve

③ Intake valve seat

④ Exhaust valve seat

PSZ Coating

⑤ Surface of cylinder head } combustion chamber side
⑥ " of intake valve }
⑦ " of exhaust valve }

Fig. 1 Ceramified Combustion Chamber

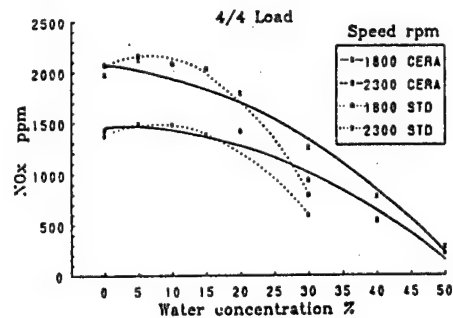


Fig. 4 Effect of Water Concentration on NOx Emission

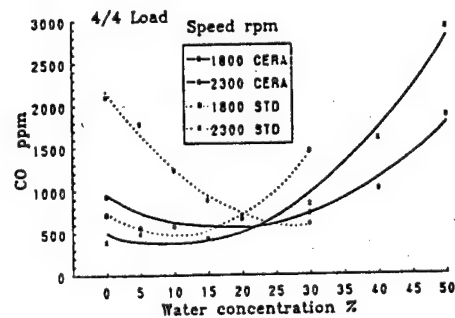


Fig. 6 Effect of Water Concentration on CO Emission

69. Study on Estimating the Change Process of Noxious Liquid
Substances in the Ocean
(FY1989-1992)

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On the easily degradable substances which were selected in the last year, biodegradation test and photoirradiation test were performed respectively.

The degraded products were separated from reaction solution and identified.

(1) Biodegradation test.

Six substances (Cumen, Isobutyl Acetate, Allyl Alcohol, Ethylbenzene, Ethyl Acetate, n-Butyl Methacrylate) were selected in the last year for this test.

The biodegradation tests were carried out according to the previous method about their aqueous solution.

Two of the biodegradation products were identified from Ethylbenzene. From all other substances one of the product was identified respectively.

(2) Photoirradiation test.

Four substances (Cumen, Ethylbenzene, α -Methylstyrene, Cyclohexanone) were selected in the last year for this test.

The photoirradiation tests were carried out according to the previous method about their aqueous solution.

One of the photoirradiation product was identified respectively.

Next year, on the above substances, biodegradation test and photoirradiation test will be performed simultaneously. The degraded products will be identified and the results will be considered synthetically.

70. Water Quality Improvement at Coastal Shore
of Waterfront Development Area

(FY 1990-1993)

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1. Overview of the Objects of This Research

Temporal stock and stabilization of nutrients at the coastal shallow area is one of the important measures for coastal water quality improvement. These measures are effective especially for shallow and narrow water area in front of waterfront development. In shallow water area and tidal-zone, there exist many kinds of flora and fauna that contribute removing organic matter from water. It is beneficial, from the energy utilization point of view, to utilize natural activity of coastal biological or ecological systems as well as natural tidal motion of water.

2. Classification of Self-purification Capacity

There are two different principles to improve coastal water quality in enclosed area, those are (a).promotion of water exchange between enclosed water and outer fresh sea water, and (b).enhancement of self purification activities along coast. In the second category, bio-filtration of shells, and organic uptake by attached biofilm are increasing spatial capacity of pollutant removal.

Pollutant removal capacity by shell is estimated by the product of following three parameters, (a) removal rate of the individual shell, (b) density of active shell per unit area, and (c) total area of the densely attached surface or bottom sediment. First parameter is measured in the laboratory. The others can be observed at the surface of various features along coastal field.

3. Experiments

Cultivation experiments were conducted to measure the bio-filtration rate of individual shell. Mytilus edulis and short-necked clam (Ruditapes Philippinarum) were selected for their wide distribution in eutrophic bays. Bottom sediment was added to the cultivation tanks. Schematic figure of the experimental tank is shown in Fig.-1. Change of particle concentration and diameter distribution was monitored with time by an electric particle counter. Typical observation results of particle volume in the tanks were shown in Fig.-2 for both shells at 22°C. Plotting the particle concentration data vs elapsed time on a semi-log chart, we can obtain a straight line. Slope of this line gives the decrease rate per unit time. Considering the water volume and the number of shell in the tank, we can calculate bio-filtration rate. For Fig.-2, particle uptake rate and (filtration rate) is estimated as 160ug/ind/min (6.8ml/ind/min) for Mytilus. Winter(1973) shows

8ml/ind/min for similar conditions.

Density of typical communities on several coastal revetments wall-surface was observed in Tokyo Bay. At the depth -1m below LWL on the straight wall in the bottom end of the bay, $10 \times 10^3 \text{ ind/m}^2$ (58kg wet/ m^2) was observed for the density of Mytilus.

4. Discussion

Using the above obtained data, we can roughly estimate feeding capacity of straight wall there as $100 \text{ m}^3/\text{d}$ per unit length (1m). Horie(1987) presented the value of $15\text{--}750 \text{ m}^3/\text{m}/\text{d}$ for straight wall in inner Tokyo Bay, which is close to our results. These estimation values varies easily with temperature, size of shell, SS/DO concentration and other environmental conditions. We need more detailed observations and experiments before applying for the actual evaluation of self-purification capacity.

references

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Winter, J.E. (1973): The filtration rate of *Mytilus edulis* and its dependence on algal concentration, measured by a continuous automatic recording apparatus, Mar. Biol., (22), 317-328

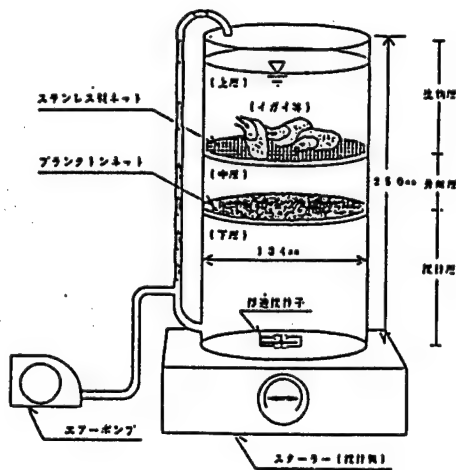


Fig.-1 Schematic figure of Labo-experiments

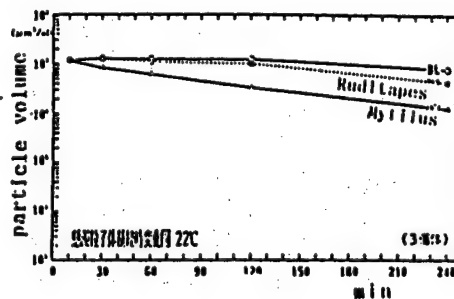


Fig.-2 Typical result of turbidity decrease with time (22°C)

71. Development of Low Atmospheric Radar
for Studying the Pollutant Transport
(FY 1990 - 1992)

Yoshihisa Masuda¹⁾, Toshio Ihara¹⁾
Kenji Nakamura²⁾, and Ken'ichi Okamoto³⁾

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Development of a pulse Doppler radar capable of measuring the wind profile from 100 m to 4 km heights above the ground was initiated by Communications Research Laboratory in FY 1990 as a three year long program.

The purpose of the development is to provide an unattended and continuously operational tool to observe wind profiles, which is useful for the research of the pollutants transportation in the atmosphere. Targets of the radar are turbulences in the atmosphere which move at the average wind velocity. The radar radiowave is backscattered by the spacial component of turbulences which have a scale of half of the radar wavelength. The wind speed is derived from the Doppler frequency shift of the radar echo signal.

The radar is operational at a frequency of 1357.5MHz and was designed as a transportable one. The frequency of the radar is higher than the usual boundary layer radar of 900 MHz. This is because of the frequency allocation situation in Japan.

The antenna and RF equipment composed of a transmitter and a low noise receiver were developed in FY 1990. In FY 1991, a controller, a demodulator and a signal processor, which form a part of radar receiver, were developed and the basic radar configuration to measure the wind profiles has been completed in the end of FY 1991.

The whole radar system developed is composed of solid-state circuits including the final stage power amplifiers of the transmitter which provides a peak power of 1.0 kW. The direction of a parabolic antenna is steerable to measure the three dimensional wind vector.

Figure 1 shows an example of the measured Doppler spectra from the air turbulences when the antenna was vertically pointed. The wind velocities are estimated from the peak of spectra. The peaks of spectra were measured up to 4.5 km with a resolution of 300 m. Figure 1 shows that the developed radar system can measure wind profiles up to 4.5 km. However, it should be noted that the maximum height of the radar observation depends on the weather conditions.

The function of measuring the temperature profiles will be introduced into the Low Atmospheric Radar in FY 1992. This function is realized by using RASS configuration, in which an acoustic antenna and an acoustic generator are added to the Low Atmospheric Radar.

Since the Low Atmospheric Radar with RASS configuration has a capability of measuring vertical profiles of the wind velocity and the temperature simultaneously, it will provide a powerful tool for forecasting the transportation of pollutant in the lower troposphere.

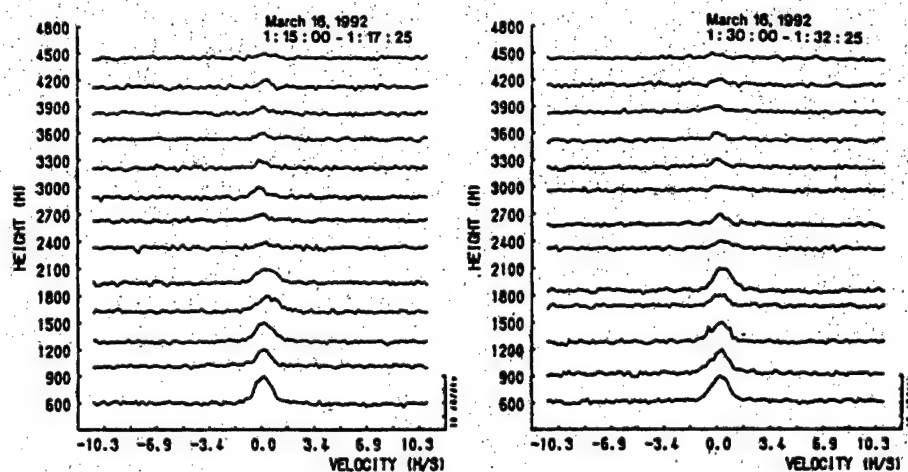


Figure 1: The height profiles of the Doppler spectra from the air turbulences

72. Asbestos Fiber Real-Time Monitor Detecting Polarized
Scattering Light
(FY 1991-1995)

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Communications Research Laboratory
Ministry of Posts and Telecommunications

We have started to study a new method of monitoring asbestos fiber aerosol. The method includes alignment of aerosol by high electric field and detection of two-orthogonal polarized scattering light of normal incident laser by the aerosol.

The alignment of fiber aerosol is adopted for making a condition of normal incidence of a laser beam to a cylindrical particle like asbestos fibers. Then, a scattered light propagates on a plane orthogonal to a length-direction of a cylinder. Photon detectors on the plane can observe at right angle the scattering light from the particle. Electric field of 1 kV/cm produces torque $8.8 \times 10^{-22} \text{ N} \cdot \text{m}$ to a cylindrical particle of 0.05-micron radius and 10-micron length which has moment of inertia $1.64 \times 10^{-27} \text{ kg} \cdot \text{m}^2$. The characteristic frequency of movement becomes 734 Hz, which will make alignment of the particles by enough speed.

We constructed an equipment to generate airborne-fibers and

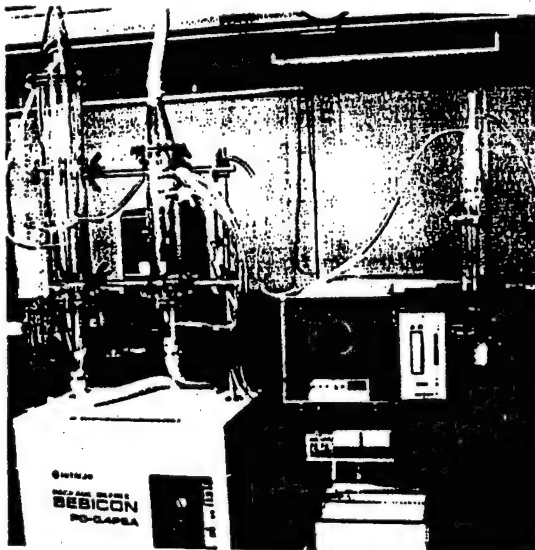


Fig.1. Airborne fiber generator



Fig.2. An image of asbestos fibers (Amosite)

an instrument to take images of the fiber aerosol by a microscope and a CCD camera. Figure 1 shows the airborne-fiber generator, in which concentration of particles is controlled by motorized valve using a signal from an optical dust monitor. A phase differential microscope, which is regularly used in the PCM method is not adequate to observation of airborne particles because of its short length between an objective lens and objects. We have applied a stereomicroscope which has a long distance between a objective lens and objects. Figure 2 shows an image of asbestos fibers (Amosite) taken by the stereomicroscope and the CCD camera.

Through computation using the Mie scattering theory, we have examined experimental conditions for discriminating between a cylindrical particle and a spherical particle by observation of scattering light including polarization. We found that measurements of polarization of the light at a scattering angle of 170 deg can strictly discriminate between a cylindrical particle and a spherical particle. Figure 3 displays polarization degree at the 170-deg scattering angle as a function of a radius of two-type of particles, where the radius of the sphere is doubled in the abscissa. The polarization of the cylinder is always positive and larger than that of the sphere which is negative as long as the radius of the cylinder is shorter than wavelength of the light.

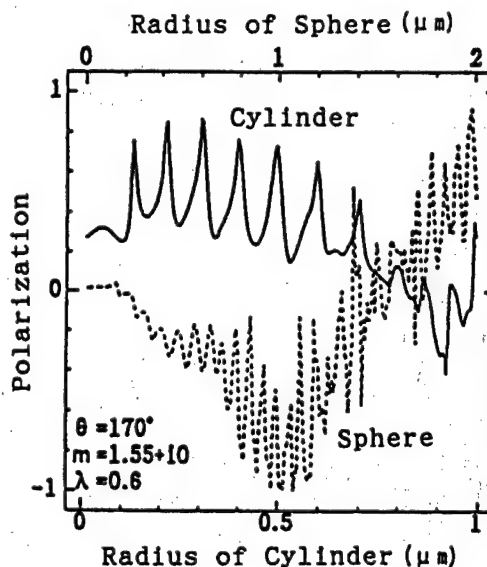


Fig.3. Polarization degree as a function of radii of a cylindrical particle and a spherical particle at a scattering angle 170 degree

73. Development of Electrical Treatment System for Oil Mists Dispersed in Factories (FY 1991 ~ 1993)

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Ministry of Labour

1. Background and Objective

In manufacturing plants, there are a variety of mist sources such as rolling and cutting processes in which lubrication oil can be vaporized and mist clouds are formed as it cools, and a painting process in which mists including volatile organic solvents are unavoidably generated.

These mists or vapors are partly condensed and collected for recycle source in some large plants, however, most are exhausted into environment and workplaces, often aggravating the condition of workplaces, and sometimes becoming a cause of air pollution.

The final objective of this study is to develop a comprehensive treatment system for mists generated in factories as described above. As a first step, we have tried to decompose vapor of VOCs (volatile organic compounds) such as toluene, because VOCs are difficult to be collected and are also very hazardous when diffused in workplaces. The means we employed to achieve this purpose was that of utilizing the SPCP (Surface Discharge Induced Plasma Chemical Process) electrode. Since an SPCP electrode can produce a plasma region having copious chemical species, it was hopeful that VOCs would be effectively decomposed by those species.

2. Experimental Setup

The SPCP electrode is made up of a cylinder of a high purity alumina ceramic with stripe tungsten films sintered on the inner surface and a tungsten sheet inside the cylinder, as shown in Fig.1. When a high-frequency/high-voltage is applied to the electrode, a surface discharge occurs on the stripe films, forming a plasma region near the inner surface.

The experimental setup consists of a SPCP electrode, an high-frequency/high-voltage power source, and a vapor generator with which liquid toluene can be vaporized at a preset concentration. Concentrations of toluene vapors before and after treating were measured with a total hydrocarbon analyzer, and then decomposition rates were calculated.

3. Summary of Results

The results obtained are summarized as follows:

- (1) When some 400 Watts of electric energy was applied to the SPCP electrode, toluene vapors of 300 ~ 2,000 ppm induced into the plasma region at the flow rate of 1 ~ 4 l/min were decomposed at the rates of up to 96 ~ 98 %, as shown in Fig.2.
- (2) After toluene vapors being treated by the plasma, tar-like substance was observed on the stripe films of the electrode. Although analyses of the substance have not been completed

yet, polymers made up of benzene nuclei and a few kinds of oxides have been observed. This substance was successfully removed by keeping the discharge in fresh air with no toluene vapors.

- (3) Thermal variation of the SPCP electrode hardly affected the decomposition rates. On the other hand, the generation of ozone decreased as the temperature rose. This means that controlling of the working temperature may be useful when ozone generation is a considerable factor.
- (4) Even argon or nitrogen was used instead of fresh air as the carrier gas, sufficient decomposition rates were obtained. This may imply that toluene molecules are decomposed mainly by high-energy electrons in the discharge plasma.

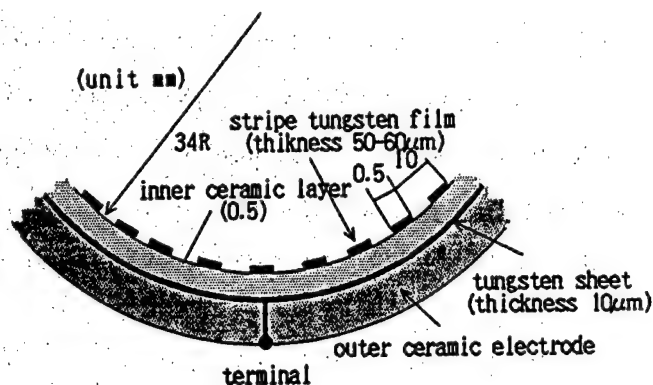


Fig.1 Cross section of the SPCP electrode

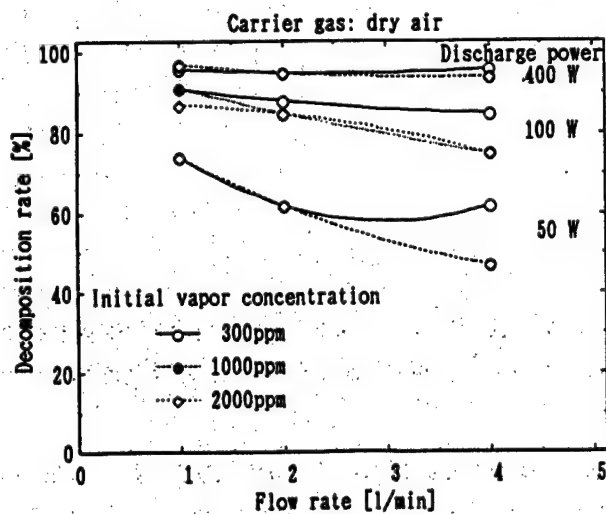


Fig.2 Decomposition rate of toluene vapor with respect to flow rate

74. Prevention of Uncontrolled Discharge into the
Atmosphere of High-Concentration Harmful Gases
Mainly Used in Semiconductor Industries
(FY 1991~ 1993)

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The present work aims to realize an industrial system which prevents the uncontrolled discharge of waste gases containing high concentration of "semiconductor gases", such as silane, into the atmosphere in the event of accidental release or unusual leakage. Those gases newly introduced to industries are chemically reactive and afraid of causing air pollution, if they would be discharged continually for a long term, because of fine powders of oxide or acidic substances generated by oxidation with air or reaction with water in the air. In semiconductor industries, those gases are handled or used in semi-sealed spaces such as "clean rooms" and gas cylinder cabinets, and those spaces are usually ventilated or exhausted so that the any leakage gases go eventually into the air through exhaust lines. Waste gases from chemical reactors are sent normally to such equipment as a toxic gas adsorber or a scrubber which renders the gas harmless, and then discharged into the air; however, the effectiveness of such equipment depends largely on good inspection and maintenance, and several accidents prove that semiconductor gas of high concentration may escape into the air from such equipment. Waste gases, either after intended use or generated by accidental leak, are thus forced to pass through the exhaust lines of a factory before going out into the air. In the proposed system, the compositions of waste gas moving through the exhaust lines are watched continuously and, when any semiconductor gas of high concentration is detected, a "valve" in the line is switched and the waste gas is forcedly led to a gas disposal unit which is specifically provided for unusual release or leakage. The valve for the system shall be developed in the coming year. One of the most important factors in the system is how to distinguish the unusual increase of semiconductor gas content in the exhaust line.

In the first fiscal year, small-scale tests were carried out to examine several factors which might affect the detection of low content of silane(SiH_4) in air moving through a pipeline. For the ease of test gas disposal by an adsorber, a closed circulating pipeline, 1-inch in diameter and 7.5m in length, was used, through which a test gas mixture was driven to move by an electric blower. Silane content in the mixture was detected by use of a commercial silane detector, then concentration-time curves were analyzed so that the effect of such factors on detecting silane was found as the velocity of moving gas mixture in the line, dimensions of gas sampling tube and silane content in the mixture. Discussions were also made on the characteristic features of electrical output from the detector which could be used as a source of triggering signal for driving the proposed system, referring the maximum rise rate of silane concentration recorded on each concentration-time curve. Results obtained were:

- 1) Recorded output of silane concentration increased with time, rather rapidly in earlier stage and extremely slowly as the output approached to a plateau which corresponded to silane content in a test mixture. While the relative value of concentration was before attaining 60% of silane content in a test mixture, concentration-time curve showed similar tendency irrespective of differences in test conditions. Thus the alarm signal which suggests an abnormal increase of silane content in the line shall be picked up within earlier stage of a concentration-time curve.
- 2) Delay time in detecting the existence of silane was independent of silane content in a moving test mixture but affected by a gas sampling system. Delay time would be estimated from that peculiar to the detector used and that caused by the sampling tube, and the latter could be calculated from mass flow rate in a sampling line and dimensions of a sampling tube.
- 3) Maximum rise rate of concentration appeared always in earlier stage of each concentration-time curve, and was found dependent only on silane content in a test mixture. It was also possible to predict silane content in the mixture from this rise rate. Then, maximum rise rate would be the most promising alarm signal for driving the proposed system.
- 4) The velocity of gas mixture moving in the line gave no effect on either delay time or features of concentration-time curves.

75. Development of Measuring Method for Concentration
of Suspended Fine Particulate Matters under $2\mu\text{m}$
in an Urban Atmosphere
(FY 1991 - 1993)

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It assumes that the air pollution on the suspended particulate matters in the atmosphere has not been improved at the present situation, because the fine particulate matters generated from a diesel exhaust may be gradually increased in the urban atmosphere.

In order to improve these problems, it should control the fine particulate matters under $2\mu\text{m}$ of particle diameter. The measurement for concentration of fine particulate matters is difficult using presently used measuring apparatus. So that, it should develop a new type of aerosol monitor to measure concentration of fine particulate matters with high sensitivity, easy operation, real time measurement and so on.

We decided to manufacture a laser-light-scattering type aerosol monitor which was consisted of a light source by laser diode having 780 nm of wave length and of a pin-photo-diode with same wave length. And we tried to get effective data before its manufacture.

First of all, the laser-light-scattering properties on the proto-type apparatus were researched by using monodisperse polystyrene latex particles generated from a ultrasonic nebulizer type aerosol generator. Three kinds of polystyrene latex particles, which were $0.305\mu\text{m}$, $0.605\mu\text{m}$ and $1.09\mu\text{m}$ of particle size, were tested to measure the relative laser-light-scattering intensities at the 5° step of each angle from 45° to 145° for the surroundings of the light scattering detector.

The results of this research for the laser-light-scattering properties on the relate of new type aerosol monitor were made clear that be able to measure the aerosol concentration of $1\mu\text{g}/\text{m}^3$ without a influence of particle size on setting the detector at the light scattering angle of 145° .

76. A Study on the Amounts of Exposure to Halogenated
Hydrocarbons by Different Routes
(FY 1989 - 1991)

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The quantitative evaluation of dermal uptake and pulmonary uptake for halogenated hydrocarbons was experimentally carried out by using nude mice. The pollution in urban air and water by these substances was surveyed by using a new device of GC-MS-ECD equipped with a headspace sampler. From these data, a simulation model to assess the dermal uptake and pulmonary uptake from air and water was investigated.

1) Distribution of halogenated hydrocarbons on dermal uptake and pulmonary uptake: The distribution of these substances within the body is an important factor for toxic effect and was investigated in mice. Most of 1,1,1-Trichloroethane (111-Tri) and Tetrachloroethylene (Tetra) was found in the liver and kidneys, and these metabolites was a little. Trichloroethylene (Tri) was metabolized and most of its metabolite was found in the liver and kidneys.

2) Measurement of 111-Tri, Tri and Tetra in urban air and water: The pollution in urban air and water by these substances was surveyed by using a new device of GC-MS-ECD equipped with a headspace sampler. Concentration of 111-Tri was 4ppb in urban air and 0.1-2.4ppb in water. Concentration of Tri was 0.3ppb in air and 0.1-4ppb in water. Concentration of Tetra was 0.2ppb in air and 0.1-2.4ppb in water.

3) Simulation of 111-Tri, Tri and Tetra by pulmonary uptake and dermal uptake: Pulmonary absorption through the lungs to concentration of

halogenated hydrocarbons in urban air was estimated by a following equation. The amount of pulmonary uptake (ug/g) was calculated by multiplying the pulmonary absorption coefficient (ug/g/h/ppm), exposure concentration (ppm) and exposure time (h). The pulmonary absorption coefficient (ug/g/h/ppm) of each halogenated hydrocarbon was 0.174 for Tri, 0.216 for 111-Tri and 0.480 for Tetra. The calculated intake values for one day in human (60kg) were 26ug for 111-Tri, 16ug for Tri and 29ug for Tetra and were compared with the allowable intake values determined by WHO for drinking water. Pollutant intake from air exceeded the allowable levels. Therefore, surveillance on air pollution caused by these compounds is necessary, regulatory standards should be discussed and techniques for pollution control developed.

Dermal uptake from partial body immersion in water pollution was estimated. The amount of skin absorption (ug/cm²) of halogenated hydrocarbons in aqueous solution was calculated by multiplying the skin absorption coefficient (cm/h), concentration of halogenated hydrocarbons in aqueous solution (ug/cm³) and exposure time (h). The skin absorption coefficient (cm/h) of each halogenated hydrocarbon in the aqueous solution was 0.0235 for Tri, 0.0125 for 111-Tri and 0.00924 for Tetra. The calculated intake values for 1 hr immersion were 0.4ug for 111-Tri, 1.7ug for Tri and 0.06ug for Tetra. These values were less than one-tenths of the allowable intake values determined by WHO for drinking water. However, in the case of that the values of pollutant in water approaches the values determined by WHO for drinking water, the amount of dermal uptake exceeds the allowable levels. Therefore, dermal uptake of those substances in water may be significant and deserves attention. And also regulatory standards should be discussed and techniques for pollution control developed.

77. On evaluation of biological effects of chlorinated hydrocarbons by an electrophysiological method.

(Fy 1990 - 1992)

Heihachiro ARITO, Masaya TAKAHASHI, Hiroshi TSURUTA and Midori SOTOYAMA

National Institute of Industrial Health, Ministry of Labor

In the 2nd fiscal year, the experiments were designed at first to look further into trichloroethylene (TRI)-induced bradyarrhythmogenesis and hypothermia observed in the previous year, and secondly to examine chronic effects of repeated exposure to TRI vapor on sleep-wakefulness and heart rate in freely moving rats. The rats had been implanted with various kinds of electrodes and thermistor and impedance-pneumographic sensors. The respiratory patterns of chest wall movement were simultaneously observed during the sleep stages with ECG, EEG and EMG recordings in the rats exposed to clean air and subsequently to 6000 ppm TRI vapor for 4 hrs. During the dark post-exposure period of 12 hrs, number of sleep-apneic (SA) episodes (>2 sec) increased together with the increased number of bradyarrhythmia (BA) episodes. Number of BA accompanied with SA also increased. However, the number of the combined BA and SA episodes were smaller than that of SA or BA, suggesting that BA is not caused by possible hypoxemia resulting from SA. Simultaneous recordings of abdominal and tail temperatures and heart rate suggested that the TRI-induced hypothermia was attributable to possible lowered set point of brain temperature rather than to imbalanced control of peripheral heat gain and loss. Repeated exposure to 100 and 1000 ppm TRI, 8 hrs/day x 5 days/wk for 6 weeks produced significant

changes in amounts of time spent in wakefulness and sleep and HR. Amounts of wakefulness, slow-wave sleep and paradoxical sleep were changed only during the exposure period. However, HR was decreased not only during but also after the exposure period. The significant decrease in HR without any change in sleep-wakefulness during the post-exposure period suggests that bradycardia is the most sensitive sign of cardiotoxicity occurring in exposure concentrations close to a threshold limit value of TRI (50 ppm).

78. Assessment of Effects of Electromagnetic Field by
Biological Monitoring
(FY 1990 - 1993)

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Development of a system to expose cells to extremely low
frequency magnetic field

There are a number of machines and appliances which deal with or consume a large amount of electric power. They usually generate strong magnetic field, especially, extremely low frequency (ELF) magnetic field, and nearby people are always exposed to it. It is necessary to clarify the effects of ELF magnetic field.

We have started the project which will lead to the assessment of the effects of ELF magnetic field by biological monitoring. In this project we are going to perform several experimental investigations of cellular effects of ELF magnetic field. This year we developed a system to expose incubated cells to ELF magnetic field which is essential in conducting these investigations. This system possesses three features: (a) strong magnetic field of up to 169mT (RMS value), (b) long-term exposure, and (c) the frequency of the magnetic field variable in the range 10-100Hz.

A number of investigations have been made on the cellular effects of ELF magnetic field, but most of them have not succeeded to obtain reliable data. This is partly because exposure dose was insufficient in these investigations. The exposure system developed in this work can realize long-term exposures of cells to strong magnetic field, that is, large-dose exposures. Using this system in experiments, we will be able to obtain clear data on the cellular effects of ELF magnetic field.

Furthermore, we can examine the frequency dependency of the effects of ELF magnetic field, using this exposure system. We may be able to draw from it valuable information on their mechanisms.

7 9 . Research on Utilization Technique of Melted Slag and Incinerated Ash Sewage Sludge

(FY 1989~1991)

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Public Works Research Institute, Ministry of Construction

Quality stabilization and improvement of melted slag and incinerated ash are necessary for promoting sewage sludge utilization as construction materials. On the other hand, there is a problem to treat and dispose a lot of construction waste which is generated mainly in urban area. Especially, excavated soil and concrete waste are generated in big mass from public works, and development on recycling and reuse technique of these wastes becomes pressing need.

The purpose of this study is to establish low cost technique grading up the final product of melted slag and incinerated ash as construction materials to combine sewage sludge with construction wastes in sewage treatment system.

Summary of the study in FY 1991 is as follows.

(1) Change of thermal characteristics in the melting process of lime-conditioned sludge.

Concrete waste or excavated soil is added for basicity (CaO/SiO_2) Adjustment in the melting process of lime-conditioned sludge.

The differential thermal analysis (DTA) showed that the melting temperature falls about 100°C , in case of the sludge basicity was adjusted from 2.9 to 1.0.

(2) The pilot test of sludge melting combined with construction wastes

The characteristics of the generated melted slag was examined as aggregate. The standard values aggregated for specific gravity, water absorption rate, and stability for sodium sulfate were achieved.

The resisting strength for abrasion of the melted slag with construction wastes is almost the same as the melted slag with silica sand. These results show that the slag with construction wastes can be used for under subbase.

It is observed that the viscosity of the melted slag with concrete waste tends to be higher than that of the melted slag with silica sand.

(3) Study on melting system to combine sewage sludge with construction wastes

In case of combining sewage sludge with concrete waste or excavated soil, it showed that the conditioning of water content and grinding of materials needs before dosing to melting furnace. And the analysis of components in concrete waste and excavated soil also needs to control the basicity of melting.

(4) Leaching characteristics of metals from melted slags

It is observed that the metal concentrations in leachates by the test method of U. S. EPA are higher than that of Japanese Environment Agency. But the metal concentrations in leachates are much lower than the standards for metals in leachate in Japan.

80 Study on Research Methods to Clarify Pollution in the
 Reef Flat Zone in Coral Reef Islands Using
 Aero-Survey and Space Image
 (Final year)
 research period 1988-1992
 by Takekazu AKAGIRI, Tamotsu SAITO
 Shinji TAKAZAWA, Kouichi MOTEGI
 Takashi HAYASHI
 Geographical Survey Institute

Introduction

In Okinawa Islands, red soil flowed out into the shallow sea area in the fringe of reef flat area. It has polluted the shallow sea area facing the coast line and consequently live corals have been damaged intensively since around 1972. It is social problems in the present, because the red soil kill live corals, pollutes sea water, disturbs to conserve natural ecology and fishery and so on. If we leave the flowing-out of the red soil to the reef flat and the sea as it continues, environments for coral reefs will be damaged intensively and continuously in future. For the reason, to establish suitable ways to stop the flowing-out of red soil and to monitor the phenomena are necessary as the most fundamental countermeasures to conserve the sea environments for coral reefs and relating life with natural landscapes.

The purpose of the study is to establish new ways to monitor polluted reef flat and surrounding sea area effectively in cheap cost in an easy way using aerial photographing system and other methods, and consequently to contribute to clarify actual conditions of polluted coral reefs. Research period is four years from 1988 fiscal year to 1991 fiscal year. This report deals with on the final part of the study. This study is sponsored by the budget for the fundamental study for the prevention of environmental pollution for national institutes by the Environment Agency.

2. Outline of the study

It is to clarify actual conditions of polluted sea area by red soil before any countermeasure to conserve the environments of coral reefs. Through the study, we tried to clarify actual conditions of deposition of red soil, marine landforms, bottom quality and distribution of many forms of life using color aerial photographs at a large scale and remote sensing images.

In 1991, color aerial photographs were taken to compare with areas polluted by red soil in Nago city in Okinawa main land (researched in 1990) and areas without pollution in Yoronjima island in Kagoshima prefecture, and to clarify surface environmental conditions of coral reefs based on the comparison with historical data through years.

The balloon photographing system was tested whether or not the system can be available for monitoring actual conditions of the distribution and change of the flow-out of red soil. Also the

relationships between deposition of red soil and critical limit conditions of existence for live coral were considered.

3. Results in 1991 fiscal year

In 1991, we researched in the area without pollution. The research consisted of aerial color photographing of clean coral reef area, subsequent analysis by photointerpretation, fieldcheck to verify the interpretation and the experimental compilation of a topographic map and an actual condition map of nature in the reef flat in the coral reefs. Based on the detailed distribution of coral reefs, a historic changes of the distribution of live corals were clarified using the results.

Using the past aerial photographs, the distribution of live corals was clarified in the area without pollution in 1946, 1977, 1984 and 1991. Also on the polluted area by red soil in 1946, 1970, 1972, 1977, 1980, 1984 and 1988.

Data of the aerial photographs were changed into digital data and the image data were analyzed and compiled into computer graphic images. Subsequently, the influence to the interpretation of sea bottom depending on the depth of sea water was made clear and absorption factor was decided. As one of results, a bird eye view map was compiled.

Trial observation using a balloon system with a camera was repeated and it was clarified that these system were available for periodical routine observations using balloon system to catch actual conditions of the distribution of live corals in the reef flat in coral reefs. As a result, the system is available, but there is a problem to be solved that to keep the direction of the camera is still very difficult, and a new system to keep the direction of the camera to take aerial photographs in good quality.

As mentioned above, based on the study through three years, we could clarify that any method is available to monitor the pollution of reef flat of coral reefs by red soil among aerial photographs, a balloon system with a camera, MSS research by aeroplane and satellite image analysis. And consequently we compiled a new manual for monitoring tidal flat of coral reef using aerial photointerpretation.

Conclusions

We studied to establish new methods to observe and monitor actual conditions of live and dead corals for three years. We examined several methods and concluded that various ways are available to research the area, among them, the balloon system is available to observe actual conditions very easily, but at the same time, still there is a problem to keep the direction of a camera.

81. Conservatin Methods of Natural Environment in Urban Rivers (FY 1989-1992)

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In urbanization of Japan, a natural river space is essentially and a conservation of it is needed. River managers have tried to conserve a natural river area. However the way to conserve a river environment was not studied enough.

In this research, we should define the characteristic of a natural river environment and propose the way to conserve a river environmet. The following investigations have been carried out.

I. Inverstigation of a natural river environment.

We investigate several types of rivers about a charactaristic of river channel, a from, a plant, a ecosystem, an amount of discharge, a water quality and a structure in order to define the characteristic of a natural river environment.

II. Proposition and assessment of the way to conserve a river environment.

We propose the way to conserve a river environment. After these experiments and field investigations, we assess it in view of a landscape, a water quality, a ecosystem and a flood control.

III. Conclusion of the way to conserve a river environment.

The following results were obtained this fiscal year.

- 1) We have been pursueing a field investigation for fish at the Ta-river which has carried out river improvement since 3 years ago. As a result of field investigations, it has cleared that concrete revetment river has less variety and smaller amounts of fish that normally inhabit rich aquatic plant habitats, which in turu, slow the river flow, in comparison with a river of natural river bank(as time passed). And also fish inhabit densities of concrete revetment river may be decreased about half in comparsion with un-improved/natural river which have aquatic plants, willow trees, rip-rap cobbles so on.
- 2) We could prove the importance of "uki-ishi-river-bed" (浮き石川床、unstable stream bed which is unsedimentary cobbles)for fish. Generally in the flood, lots of fish are flowed to down stream by flood because most fish can not resist the flow velocity at "shizumi-ishi-river-bed" (沈み石川床、stable stream bed which is sedimentary cobbles)which has not or cattail plants zone of fish using a casting cover net form senter of river in in flood at the Ta-river which is many uki-ishi-river-bed(because fish take refuge in to the uki-ishi-river-bed).

- 3) Present in Japan, river improvement construction has promoted activity in construction of concrete remetment on the river side(which has come into wide use)in order to protect scouring caused by flood. However, on the other hand, river improvement produces an evil influence on the habitat of fish, due to the decreasing of rapids, deep pools and aquatic plants associated with these improvements for the above reason. We madean effort and carried out to improve the Naturally Diverse Construction Methods "多自然型河川工法" which is able to inhabit many kind of fish according to rehabilitate inhabitable environment for fish.

Table-4 List of sampling pisces in Ta-river

採捕魚類一覧表 (田川)

| Species name (Kinds of fish) | 1990 years | | | | 1991 years | | |
|--|------------|------|------|------|------------|------|-------|
| | 6/12 | 7/23 | 9/8 | 11/5 | 1/27 | 7/25 | 8/31 |
| スナギタメ Lampetra (Entosphenus) tridentata | | 1 | | 20 | | | |
| マス Oncorhynchus masou masou | 4 | | | 1 | | 1 | マサマサ |
| フナ Plecoglossus altivelis | 18 | 10 | 1 | | 1 | 1 | 6 |
| コイ Cyprinus carpio | 2 | 4 | 1 | 36 | 2 | 1 | |
| キナガサ Carassius carassius buirgeri | 5 | 10 | 10 | 14 | 3 | | 4 |
| タナゴ Rhodeus (Achellognathus) morioakae | | | 2 | | | | |
| ウグイ Leuciscus hakonensis | 28 | 50 | 66 | 238 | 84 | 170 | 807 |
| フナコ Phoxinus phoxinus | | | 2 | 1 | 3 | | |
| タイザン Zacco platypus | 20 | 9 | 14 | 8 | 12 | 14 | 27 |
| カマメ Zacco temminckii | | 1 | | | | | |
| カマナ Pseudogobio (Pseudogobio) esocinus | | 21 | 23 | 35 | 1 | 1 | 42 |
| タモロコ Gnathopogon elongatus | 3 | 54 | 75 | 405 | 80 | 2 | 121 |
| モロコ Pseudorasbora parva | | 3 | 5 | | | | 12 |
| ドジョウ Misgurnus fossilis anguillicaudatus | 1 | 27 | 39 | 50 | 3 | | 32 |
| ヤマドジョウ Cobitis (Cobitis) biwae biwae | 10 | 29 | 100 | 22 | 4 | 1 | 43 |
| ホトケドジョウ Lefua costata | | 12 | 17 | 18 | | | 2 |
| マナズ Silurus (Parasilurus) asotus | | 3 | 7 | 2 | | | 1 |
| ヨシノボリ Rhinogobius brunneus | 3 | 7 | 50 | | 20 | | 3 |
| Total 18 species | 10種 | 15種 | 15種 | 13種 | 11種 | 8種 | 13種 |
| Sampling number | 94匹 | 241匹 | 412匹 | 850匹 | 213匹 | 191匹 | 1101匹 |

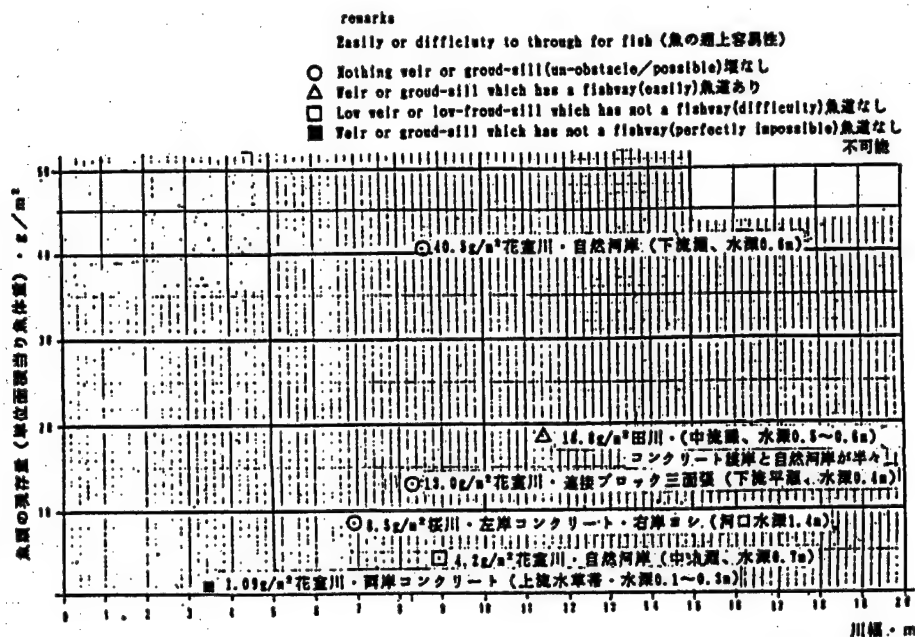


Fig-1 Average inhabit densities of river pisces (total fishweight water surface area) 魚類の平均生息密度 (総魚体重/水面積) (winter season)

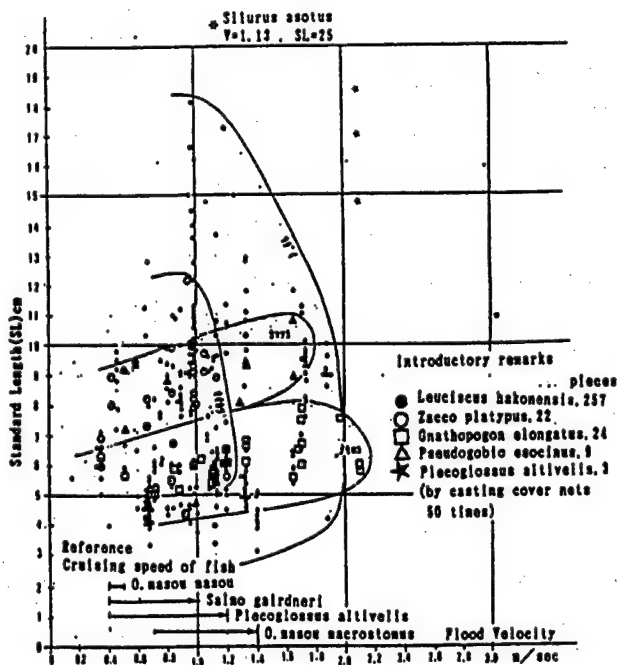


Fig-2 Sampling of fish and flood velocity of the point in "Uki-ishikasyo", unstable stream bed which is unsedimentary cobbles.

浮き石帯における魚類の採捕とその場の洪水流速

82 Planning Technique for Residential Districts with Full of Amenity and Conserving Natural Environment (FY 1991-1993)

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Kazuhisa Iki
Katsushi Satoh
Nobuhiro Yamahata
Masamiki Ohhashi

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Recently many housing districts are developed in hilly or even mountainous areas in or near cities. Planners wish to conserve the natural environment and to create there a housing environment with full of amenity for residents at the same time. But in almost all cases, the districts are developed into the excavated and flattened land to make it easy to plan and execute, and to reduce the construction cost. But if you see the fact that the trees planted after completion of buildings often grow bad because of mismatch to the land conditions and cannot serve as amenity resources, you can understand that the reduction of initial cost does not mean the reduction of cost for maintenance of amenity level.

We have already developed two basic models: one for prediction of natural environment potential of land interpreting the suitability of land soil for plants and another for evaluation of landscape composed of plants and buildings from viewpoint of amenity for residents.

The natural environmental potential of land signifies the suitability of land for the tree. According to the calculated potential of a land the trees planted there grows better and show a stronger vitality.

The evaluation model is composed of two factors; one is a model to make a series of visual images that the future residents will see on the pathways when they walk around in the planned residential district and another is a model to evaluate the plan on the basis of the impressions of residents.

This study is to create a planning technique for residential districts with full of amenity and conserving natural environment; by joining these two models, by widening the application region and by giving the easiness of use in practice.

In the fiscal year 1991, following subjects were studied;

1. Improvement of the prediction model for natural environment potential of land soil by applying fuzzy method.

The introduction of fuzzy method seems very useful for extension of applicable region of this model, because the component factors we can use for the model do not always show a perfect independence and in practice there often arrives some lack of data. The fuzzy method introduces statistically relative functions between factors and can give the results even when the

given data are incomplete.

However, statistically significant number of complete data are necessary to introduce the relative functions between factors used in the model, because the modification of model based on the incomplete data provokes a risk to give a certain error even when the data is complete.

2. Verification of applicability of the model to wider region

The master tree species serve as a scale for measurement of natural environment potential of the concerned land. According to the regional conditions, the dominant tree species of the residential district vary, and the natural environmental potential of a land should be converted according to this difference of dominant tree species.

To extend the applicable region of the prediction model of natural environment potential, we chose "Sendai", a city in north eastern region of Japan and "Kobe", a city in south western region of Japan. The extension of the applicable region of the model requires two works; one is to find out a convert function between the two tree species and the other is to introduce the factor of difference of climate and land soil conditions into the model. We carried a series of surveys to find out the residential districts in each region appropriate to verify the applicability of the model, where we can find out two master tree species neighboring each other in a site. From the comparison of the vitality of two tree species we will obtain the convert function between the two species.

The consideration on the difference of climate and land soil conditions asks to take into account the situation of stock of these data in every region in Japan on which we are planning to conduct a survey.

3. Improvement of landscape evaluation model

The basic model can compose a series of images in a range of about 10m from residents. We improved it by adding the software to lay a rear scene and a background scene under the first image. With this integrated image, the planners can seize better the result of their development plan.

To obtain the numerical evaluation of these images, we are planning a survey about the impression of residents on the composed image and eventually the impression between the image composed by computer and the real landscape.

4. Collection of physical effects of plants

The evaluation of development plan from viewpoint of visual impression has a risk to permit for the planners to ignore the physical effects of plant on the residential districts. To compensate this problem we wanted to give the planners the physical data of the plant effect on the district and we started to collect the numerical data of the physical effect.

83. The Study on Technology to Reduce The Noise Generated by Construction Machine

(FY 1990~1993)

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1. Introduction

In surveys on the realities of complaints about construction noise, many more complaints pertain to work performed with rock drills than to any other type of specified construction work.

Under these circumstances, noise from hydraulic breakers must be reduced, though late, to decrease complaints about noise in construction work. In FY 1991, we implemented measures to reduce noise from hydraulic breakers on the basis of test results of the previous fiscal year and examined their effects.

2. Purpose of Study

The purpose of this study is to clarify the noise generating mechanisms of hydraulic breakers with mechanisms to generate impulsive noise by impact, and see how to reduce this noise and establish low-noise hydraulic breakers.

3. Method of Study

3.1 Fabrication of Prototype Noise Reducing Components

When we investigated the state of noise generation by hydraulic breakers in FY 1990, we found that there was a tendency for sound to radiated from the vicinity of the chisel impact in the interior of the breaker, and the vicinity of the window of the side bracket, and then the whole of the breaker itself with the chisel part as the center.

To reduce sound radiated from the breaker, it is necessary not only to interrupt sound emanated from the surface of the breaker but also to suppress the vibration of the breaker itself. So, in FY 1991 we checked for the effect of noise reduction by surrounding the surface of the breaker with a damping material and wrapping this with a sound proof steel sheet cover in expectation of its sound insulating effect.

We used urethane rubber as damping material in consideration of its strength and workability besides its damping effect and used SS400 for sheet steel.

3.2 Method of Noise Measurement

Ambient noise was measured at a height of 1.5m, and in all four directions 7m and 15m from the hydraulic breaker when breaking concrete slabs and granite on the assumption of actual breaking work and we analyzed noise levels and $1/3$ octave frequency.

4. Results of Study

Table 1 shows the results of the ambient noise measurement in Case A-1 before initiating noise

reducing measures and Case G-1 after noise reducing measures by the soundproof cover and the damping material. The average value of noise at the 7-m point was reduced by about 7 dB in breaking concrete slabs with a point chisel and about 7 dB in breaking granite with it.

The following became known from our survey results in FY 1991:

- 1) Noise reduction by about 3 dB is possible by using the prototype soundproof cover we fabricated.
- 2) Noise reduction by about 5-7 dB is possible by combined use of the soundproof cover and the damping material.

5. Problem to Be Solved Hereafter

We believe that in the future, it will be necessary to study this in order to achieve structures that can withstand actual use and make improvements so as to reduce noise even more without impairing workability.

Table-1 Effect of Noise Reduction

Unit: dB(A)

| Case | Type of Impact | 7 m | | | | | 15 m | | | | |
|----------|-------------------------|--------------|-------------|-------------|------------|---------|--------------|-------------|-------------|------------|---------|
| | | Front, right | Front, left | Rear, right | Rear, left | Average | Front, right | Front, left | Rear, right | Rear, left | Average |
| Case-A-1 | Breaking concrete slabs | 97 | 95 | 95 | 96 | 96 | 97 | 98 | 98 | 99 | 98 |
| Case-G-1 | Breaking concrete slabs | 88 | 89 | 89 | 89 | 89 | 79 | 80 | 80 | 81 | 80 |
| Case-A-1 | Breaking granite | 100 | 99 | 98 | 97 | 99 | - | - | - | - | - |
| Case-G-1 | Breaking granite | 90 | 91 | 92 | 93 | 92 | - | - | - | - | - |

Case A-1: Before noise reducing measures
Case G-1: After noise reducing measures

84. Researches on the Method to Evaluate Lotic Environments Based on
the Biological Condition of Macrobenthic Invertebrates in Japan
(FY 1989 ~ 1991)

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Although macrobenthic invertebrates are regarded as a good indicator of the lotic environment, evaluative techniques using these macrobenthic invertebrates have not yet been standardized because of methodological disunity, taxonomical difficulties involved.

Then, in the present study, in the light of the biological water quality score system now under way in England and in consideration of the present situation of taxonomy and the biological condition of macrobenthic invertebrates in Japan, we have been examining possible standardization of evaluative techniques for the lotic environment using macrobenthic invertebrates, which are practicable even on the part of environmental institutes of local government which lack in biological experts.

In the previous report, we examined sampling methods and clarified that the one minute-sampling method by kick-sweep using D-frame net was practicable for the biological condition of macrobenthic invertebrates in Japan.

In the present report, from the relation between data on 114 samples (48 spots) of macrobenthic invertebrates in 20 rivers of Kanagawa Prefecture, Isikawa Prefecture, Hyogo Prefecture and Fukuoka Prefecture, which we sampled in the past 3 years and degrees of river water quality organic pollution at the same spots, we set up scores for each family of macrobenthic invertebrates and examined the validity of these scores in comparison with the evaluative results with the surber sampler method in conventional use.

The results can be summarized as follows:

- 1) Pollution index (PI) of Pantle & Buck (1955) at each sampling spot according to the surber sampler method was 3.6 (ps) and 1.0 (os) at maximum and minimum, respectively.
- 2) According to the water quality index (WQI) of Yoshimi et al. (1982), river organic pollution tended to be low and high at upper and lower reaches, respectively and was lowest and highest in -1.88 and 4.52, respectively.
- 3) From WQI values and the biological condition of macrobenthic invertebrates, pollution index by families was calculated on a total of 73 kinds of macrobenthic invertebrates (71 families and 2 classes) and index values calculated were ten-sected. Scores were set up on these 73 kinds of macrobenthic invertebrates in such a way as to give score 1~10 to kinds with minimal-maximal pollution index by families, respectively (Table 1).
- 4) ASPT (average score per taxon) values at each sampling spot determined from scores tended to be high and low at upper and lower reaches, respectively, being highest and lowest in 7.41 and 2.00, respectively. The above values showed a small seasonal variation.
- 5) Similar correlation at a level of significance of 5% was noted between ASPT values and PI values in every season.

The above results suggested the practicability of the evaluation of river water quality by ASPT values using scores on the basis of a rough classification at the levels of family.

The score system in this report which was based on the data in 20 rivers of four prefectures, has need for more data of the various biological condition of macrobenthic invertebrates to be available for all rivers in Japan.

Table 1 Score system

| Order | Family | Score | Order | Family | Score |
|---------------|--------------------|-------|----------------|-------------------|-------|
| Ephemeroptera | Siphonuridae | 8 | Coleoptera | Uenoidae | 10 |
| | Isonychiidae | 7 | | Limnephilidae | 7 |
| | Heptageniidae | 7 | | Lepidostomatidae | 9 |
| | Baetidae | 6 | | Sericostomatidae | 7 |
| | Leptophlebiidae | 7 | | Odontoceridae | 9 |
| | Ephemerellidae | 7 | | Molannidae | 9 |
| | Caenidae | 6 | | Leptoceridae | 7 |
| | Potamanthidae | 7 | | Gyrinidae | 6 |
| | Ephemeridae | 7 | | Hydrophilidae | 7 |
| Odonata | Polymitarcidae | 5 | Diptera | Psephenidae | 6 |
| | Calopterygidae | 8 | | Dryopidae | 7 |
| | Epiophlebiidae | 8 | | Elmidae | 6 |
| | Gomphidae | 7 | | Ptilodactylidae | 8 |
| | Cordulegasteridae | 6 | | Lamprolidae | 8 |
| Plecoptera | Corduliidae | 5 | Diptera | Tipulidae | 7 |
| | Taeniopterygidae | 10 | | Blepharoceridae | 10 |
| | Nemouridae | 8 | | Deuterophlebiidae | 10 |
| | Capniidae | 9 | | Psychodidae | 6 |
| | Leuctridae | 10 | | Dixidae | 8 |
| | Peltoperlidae | 9 | | Simuliidae | 6 |
| | Perlodidae | 9 | | Chironomidae | 3 |
| | Perlidae | 7 | | Tabanidae | 9 |
| Hemiptera | Chloroperlidae | 10 | Tricladida | Athericidae | 8 |
| | Aphelocheiridae | 6 | | Dugesidae | 6 |
| Megaloptera | Corydalidae | 7 | Mesogastropoda | Pleuroceridae | 6 |
| Trichoptera | Stenopsychidae | 8 | Basomatophora | Lymnaeidae | 3 |
| | Philopotamidae | 8 | Unionoida | Physidae | 1 |
| | Psychomyiidae | 8 | | Ferrissidae | 3 |
| | Polycentropodidae | 7 | | Unionidae | 6 |
| | Hydropsychidae | 6 | Veneroida | Corbiculidae | 6 |
| | Rhyacophilidae | 8 | (Oligochaeta) | | 2 |
| | Glossosomatidae | 7 | (Hirudinea) | | 2 |
| | Hydroptilidae | 6 | Amphipoda | Gammaridae | 7 |
| | Limnacentropodidae | 9 | Isopoda | Asellidae | 2 |
| | Phryganopsychidae | 6 | Decapoda | Sphaeromidae | 9 |
| | Phryganeidae | 8 | | Potamidae | 8 |
| | Bruchycentridae | 9 | | | |

8 5. Study on Preservation and Mechanism of the
Stabilization of Coral Reef Ecosystem
(FY 1989 - 1991)

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In order to clarify the nature of recovery of coral community, and the relationships between the recovery and environmental factors, experiments and researches as follows were carried out at the Yaeyama Marine Park Research Station on Kuroshima Island and its vicinity, in Yaeyama Group, Ryukyu Islands, 1989 to 1991 fiscal years.

1. Region level survey

8 characters as follows were examined at 91 stations in the survey area (the Sekisei Lagoon and its surroundings)

1. coverage of living corals;
2. time of extinction of coral community;
3. growth type of living coral community;
4. density of A. planci;
5. density of feeding scars of the starfish;
6. depth;
7. nature of bottom;
8. maximum diameter of table-type Acropora in each station.

There are several stations with their coverage of living corals increased during the several years, and the recovery of coral community has advanced gently. However the stations of Acropora spp. as the dominant species are still very few, and coral coverage are less than 20% in many stations, just same as the results of the last several years. The distributed area of A. planci was observed from south area of Ishigaki Island to South area of Taketomi Island, and east area of Kuroshima Island, in 1975. In 1981, the population of A. planci occupied southern half of the Sekisei Lagoon. A. planci was distributed in Yonara Strait, east, west

and south area of Kuroshima Island, and the area of between Taketomi and Kohama Island, in 1984.

The populations of corals were distributed in northern reefs of Kayama and Taketomi Islands. But the population density of A. planci decreased from 20 individuals per 100m² in 1985 to 10 individuals per 100m² in 1986, and 1-2 individuals per 100m² in 1987. After that A. planci was observed 0-1 individual per 100m² from 1988, in constance. Outbreak of the starfish in survey area therefore, seems to have been almost finished. The recovery of coral community in the survey area is still far from the normal condition, and the degree of recovery is much different station by station, as in condition of the last several years.

From the analysis of depth, substratum, wave action, and current velocity at 91 stations mentioned above, it is clear that the coral recovery never correlated to those factors.

Survey of amount and component of drift sediments, and amount of silt was taken place at 10 stations out of 91 stations mentioned above, chosen by the consideration of coral recovery and condition of surrounding sea water. Furthermore, survey of sedentary organisms was also taken place at the 10 stations by using test panels made of skeletons of massive corals.

The analysis shows that there are no correlations between coral recovery and each of the surveyed factors.

2. Community level survey

In order to research changes or developments of coral communities, species and size of corals, and coral coverages were examined in each 100 permanent quadrats of 1m X 1m at every eight permanent survey points, for two years, at intervals of six months. At every eight points, data of five examinations (Jan., Jun., & Dec. in 1990, and Jun., & Nov. in 1991) are similar each other. Therefore, there are no essential changes on coral communities in all survey points, during the last two years.

From the analysis of changes of the number of colonies, growth scores, and coverages of corals during last two years, it is clear that all survey points except Pt. 5 have no essential changes, or almost so, and that coral community at Pt. 5 has grown gradually.

Each of the surveyed coral communities looks like a rather stable community, during a short period such as the intervals of this survey. However, from the analysis of every corals in all quadrats, it is clear that they change dynamically as time goes by.

Great amounts of changes are seemed to be not due to the recruitment

of coral larvae, but due to the fragmentations of every corals. The fragmentations may take place by heavy wave actions or strong currents while stormy weather.

On the genus level survey of small-sized colonies ($d=2-5\text{cm}$) in 20 permanent quadrats in every eight points, number of the small-sized colonies is not directly related to the amount of recruitment of corals. However, the analysis of small-sized colonies of Acropora and Pocillopora shows the importance of upper surface of substrata for the recruitment of corals.

3. Colony level survey

Growth experiment of 4 species of corals (Seriatopora hystrix, Montipora digitata, Acropora formosa and Anacropora spinosa) was carried out for a year approximately, using coral plantation panels, at 3 experimental points, where environmental conditions were different. Each transplanted colony was photographed for measurement at intervals of 2 months. Temperature, salinity and turbidity of sea water have been also recorded by data loggers at each point for the analysis of correlations between coral growth and non-biological environmental factors.

Results are that coral growth indicated maximum quantity between August and December. It was not appeared that turbidity prevented coral growth.

It was supposed that intense daily range of water temperature prevented growth more than turbidity.

Conclusion

Although almost all regions were damaged by outbreak of population of Acanthaster planci, to no traces of corals in the survey area, there are many moats or sub-areas with the recovery of coral communities of much different degree.

The cause of very low or no recovery of coral communities may be due to the following three reasons, 1: Absence of recruitment of coral larvae, 2: Absence of coral colonies based on the strategy of fragmentation, 3: Absence of substrata where the coral larvae recruit.

The rapid recovery of coral communities on these sub-areas may be induced by artificial plantation of coral fragments.

86-I Regenerable Filter Trap Oxidizer and Oxidation
Catalyst System for Diesel Particulate Control
(FY 1990 - 1993)

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Diesel exhaust particulate, which is one of the component of the contamination in the air, need an urgent countermeasure, because it is causing suspended particulate contamination, photo-chemical smog and other elements of air pollution, and it makes void a catalyst and EGR effects for NOx.

Filter trap oxidizer method is one of the most promising countermeasure of diesel exhaust PM (particulate matter). This method uses DPF (diesel particulate filter) placed in the exhaust section of the diesel engine mounted in the car. PM is once collected in the DPF, and burned in the suitable condition for recombustion. By the recombustion, collected PM is changed to gas phase and emitted, and the DPF is regenerated simultaneously.

This study succeed the "Diesel Exhaust Particulate Control by Filter Trap Method" which showed possibility of particulate control by filter trap method and ended in FY 1987, and aimed to the method to practical use. This study plan is composed of two parts, one is "study on prevention technique of thermal stress destruction of DPF element" which aim to recombustion in uniform temperature. And the other is "study on the technique to find out the optimum regeneration timing" which aim to show the optimum recombustion timing with monitoring technique of the quantity of trapping particulate on DPF.

In the "study on prevent technique of thermal stress destruction of DPF element", the regeneration method by auxiliary heater and the engine exhaust flow was selected by the result showed in the former report. The regeneration in the uniform temperature was sought after and temperature

distributions in the filter in the recombustion process were measured. And effects of DPF property and adiabatic property of DPF holder on temperature distribution were investigated. Then conclusions as follows were made clear in this fiscal year.

1. In the case of regeneration by the auxiliary heater and the engine exhaust, the temperature in the filter largely depend on the exhaust flow rate. Especially, highest temperature position move with the flow rate along the axis direction.

2. In the above mentioned case, using effective adiabator as the holder of filter is effective for uniformization of temperature in the filter.

3. In the regeneration of above mentioned, CH2 filter (porosity 50 %) is favorable than MF filter (porosity 90 %) about the temperature distribution. It was considered that a filter having high thermal conductivity and large heat capacity was effective for uniformization of temperature in the filter in regeneration.

In the "study on the technique to find out the optimum regeneration timing", monitoring technique of the collection quantity of particulate on DPF by measuring pressure drops of DPF and flow through element was proposed. And fundamental property of SOOT SENSOR which was measurer of the accumulated quantity of particulate on DPF was investigated. Then the results of this theme in this fiscal year were as follows.

1. The relationships between pressure drop and flow through rate of wall flow filter and flow through element show the similar downward convex curves. Those curves can be simulated by quadratic curves with good precision.

2. In the case of particulate accumulated filters, relationships between flow through rates and pressure drops can be simulated by quadratic curves too. And, increase of accumulated particulate shows small decrease of quadratic coefficient and increase of linear coefficient.

3. Using the results of above mentioned, particulate accumulated quantity on filter can be monitored by means of continuous measurement of pressure drops of filter and flow through element.

4. Fundamental ability of soot sensor (measuring device of particulate on filters using microwave absorption of soot) were measured and made clear.

5. It was found out that exhaust temperature and particulate accumulated quantity had a complicated effect on the soot sensor out put.

86-II. Regenerable filter trap oxidizer and oxidation catalyst system for diesel particulate control (FY 1991 - 1993)

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It is thought that it is indispensable to adapt exhaust cleaning devices in the exhaust system in order to achieve the sharp reduction of both NOx and particulate emissions. The importance of the study on feasibility and resistance performance of exhaust cleaning devices is further increasing. It is said that, in future diesel vehicles, the rate of soots in diesel particulate emissions will decrease and the rate of soluble organic fraction (SOF) will increase. An oxidation catalyst system can clean SOF and has a lot of merits such as a low flow resistance. Therefore, the oxidation catalyst system is one of the most feasible means of cleaning exhaust gas in diesel vehicles.

The objective of this study is to investigate the feasibility of cleaning diesel particulate emissions by the oxidation catalyst system, to establish the technical ground to achieve the long range target of the particulate matter regulation, to clarify the various problems for practical oxidation catalyst systems and to find the countermeasures to these problems. In this fiscal year, the statistical behavior of main factors which have the influence on the catalyst performance has been investigated in vehicle driving tests. The influences of composition performance of oxidation catalyst systems with different types of catalyst have been analyzed. The results as follows have been obtained.

1. Analysis of behaviors of engine speeds, loads and exhaust gas temperatures in the real driving condition

The relation between various real driving conditions and exhaust gas temperatures have been investigated. As a result, the characteristic of engine driving behaviors has been statistically clarified about the diesel truck in 3 types of road; a general highway, an ascending road and an expressway.

2. Analysis of soots, SOF and sulfates in particulate matters by thermogravimetric analysis

In order to analyze the conversion rate of SOF by oxidation catalysts, measurement methods of soots, SOF and sulfates in particulate matters have been developed. As a result, the tendencies of contribution rates of the compositions in particulate matters have been understood by this method. This method is effective for the analysis of conversion performance of SOF by oxidation catalysts.

3. Study on the characteristics of cleaning particulate matters by a flow through type oxidation catalyst

When the sulfur concentration in light oil is zero, a flow through type oxidation catalysts is an effective device for reducing particulate matters in all of driving conditions. In order to put this catalyst to practical use, it is necessary to reduce the sulfur concentration in light oil and to develop the catalyst which has low oxidation activity for SO_2 with oxidation activity for SOF kept high.

87. Development of New Wastewater Treatment Technologies for Environmental Water Quality Control

(FY 1988~1991)

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The pollution of natural water bodies, especially lakes and reservoirs, in Japan is becoming more serious mainly due to increased discharge of domestic wastewater, so that the water quality does not meet the requirements of various water uses such as municipal water supply, irrigation, fishery and pollution control. This project consists of three sub-projects and one of them was completed last year. The results of the other two sub-projects are summarized.

Part 1: Development of advanced treatment processes and system for domestic wastewater control

The object of this study is to develop the new Johkasou systems with advanced treatment processes, which can meet higher requirements for satisfactory domestic wastewater management in the unsewered areas. A comprehensive study on advanced wastewater treatment and excess sludge treatment/disposal was performed. In addition, a feasibility study on domestic wastewater management system was done in a model area with Johkasou systems to achieve non-discharge of treated wastewater and excess sludge from the area.

Field surveys of 4 small scale Johkasous for individual household and a middle scale Johkasou for a small community with 33 households showed that the use of disposers resulted in increase of wastewater quantity and pollutant load by 10 L, 15gSS, 17gBOD, 13gCOD, 1.4gT-N and 0.14gT-P per day. However, insignificant change of effluent quality except increase of SS concentration was observed in the middle scale Johkasou under frequent excess sludge removals. Required volume for small scale Johkasous and some necessary improvements in structure and maintenance for middle scale Johkasous were proposed to accept wastewater from disposers.

An improved type of small scale Johkasou with a peak-cut chamber and return of treated wastewater was examined to remove BOD and T-N, and proved to produce the effluent with BOD and T-N less than 20mg/L. However, further examination was required to obtain stable removal efficiencies of these items. Several kinds of unit processes were evaluated to examine the feasibility of application in middle and large scale Johkasous. Intermittent aeration of the activated sludge process under DO and ORP control produced higher removal of BOD, T-N, T-P and so on, and ultra membrane filtration improved very excellently removal efficiencies of BOD and SS. Water quality standards for emission and reuse of treated wastewater were set and some advanced wastewater treatment systems to meet these standards

were proposed.

The quality and quantity of excess sludge generated in several kinds of Jookasous were evaluated to obtain fundamental information for sludge treatment and disposal. The advantageous effects of saponin on oil removal and decrease of adverse effects by oil were confirmed through experimental studies of the activated sludge process. Filtration units with unweaved cloth were developed and evaluated in semi-batch and continuous modes to thicken excess sludge with low energy consumption.

The feasibility study on a proposed domestic wastewater management system in the model area led to the conclusion that non-discharge system of treated wastewater and excess sludge as well as rain water can be established using Jookasou systems which were proposed in this study.

Part 2: Development of advanced treatment technologies for secondary treated municipal wastewater

There are two main objectives in this part. One is the establishment of the qualitative and quantitative analytical methods for the trace organic materials that cause the odor and color in the effluent of the municipal wastewater treatment processes. The other is removal of the odor and color from the secondary effluent.

Field survey at two sewage treatment plants were carried out to determine the seasonal variation of odor, color and residual organic matters in raw wastewater and treated effluent. The flux of odor and color from each unit process such as a sludge thickener at other two treatment plants was also investigated. It was shown that the threshold odor numbers (TON) of the raw wastewater were about 1,000 in winter and above 3,000 in summer, and the TON of the effluent from the conventional activated sludge process were from 50 to 130. The values of color were 40-80 units in the wastewater and 20-40 units in the effluent. The TOC values were 10-30 mg/L in the wastewater and 5-10 mg/L in the effluent. It was found that the flux of odor among the treatment processes was mainly associated with the flux of solid. The flux of color showed a little variation.

The combination of ozonation process and activated carbon adsorption process was investigated for the removal of odor, color and organic compound from the secondary effluent. This process could reduce the TON from 50-200 in the influent to 5-30 in the effluent, mainly at the packed activated carbon bed process. It was supposed that the deodorization in the activated carbon bed were due to biological removal. And the color units were reduced from 10-40 to 1-9, mainly by the ozonation process. The high removal efficiency was kept up to the end of the experiment (20,000 times of the volume of the activated carbon bed) and were shown to be sufficient in this combination process.

88- I . Prediction of Wind-driven Currents and Mass Transport in an
Enclosed Sea
(FY 1988~1991)

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The main aim of this study is to develop a simulation model for an accurate prediction of mass transport caused by the combined action of wind and tide in an enclosed sea. The hydraulic experiment using a wind-tunnel basin and field experiments in the Harima Sea were carried out in order to investigate the generation mechanism of the wind-driven current with vertical structure and to understand the fundamental nature on the mass flux which is caused by the tidal and wind-driven currents.

The following research were carried out in this study.

1. An one-dimensional tidal model of the Seto Inland Sea was developed. This model gives tide, tidal volume-transport, and wind-driven current through the Seto Inland Sea; these results were verified from the field observations.
2. A two-layer tidal model of the Harima-sea was constructed in order to study the three-dimensional structure of wind-driven currents in the Harima-sea. Boundary condition of this model were given from the one-dimensional model. The calculated results represent an existence of the effect of the Earth's rotation. The waters in the sea flow to the right-hand side in the upper layer, and to the left-hand side in the lower layer facing the leeward. This flow structure was verified from the field observations.
3. Harima-sea is composed of narrow straits and a wide embayment forming a "strait-embayment system". In the system, tidal currents through the straits are much stronger than those within the embayment. The hydrodynamics in the system is strongly nonlinear and mass transport processes are advection rather diffusion. We conducted a drogue tracking experiment in the Harima-sea and found a new type of transport mechanism; a tidal-jet from the strait transforms into a vortex and this vortex

carries water mass effectively to the center of the embayment.

4. Wind induced drift current under water current condition are investigated by using a wind-tunnel basin $W60\text{cm} \times D1.2\text{m} \times L50\text{m}$ with a water circulation pump system. Vertical wind profiles were measured under the conditions with and without water current, by using a pitot tube and pressure transducer. Further, wind induced drift current profiles were measured by using a fiber-optic laser velocimeter. Variations of friction velocity and roughness length at current water surface with increaseing fetch were estimated from the wind velocity profiles near the water surface. Although the wind waves generated in the basin grow with increaseing fetch, the values of friction velocity and roughness length gradually decrease with fetch. The relation between the friction velocity, u_{*a} , and the wind speed, U_{10} , under water current was found to be smaller than that under no water current. Influence of wind is propagated under current water deeply, and wind induced drift current occur in the region more than half of the depth of water.

88- II Prediction of Wind-Drive Currents and Mass Transport in an
Enclosed Sea
(FY 1988-1991)

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This study is aimed to research the influence of wind to the current and mass transport, and to improve their prediction in enclosed seas. Tokyo Bay was selected as model sea. As this year is the last year of the study, we tried to examine the prediction through the drifting experiments. However the test-run of the numerical model, which was made in the former year, was not be able to finish according to the instability of the computation. The sem-empirical model, which was based on the current observation data, was adopted instead of the numerical model.

In the experiments, the floats which drift in the surface layer sinking about 30cm to avoid the direct force of wind, were released at the same time from 4 stations and traced from 9:00 to 15:00, on December 18th and 19th. For the reference, the currents were observed at 4 layers in each station and the wind at 30m in the Tiba-Light during 15 days from December 9th to 24th.

For the directions, the trajectories of floats were agreed with the progressive vector diagrams (PVD) of the surface currents shallower than 3.0m, but for the length their differences were large. The trajectories disagreed both in direction and length with the PVDs of the deeper layers than 3.0m because their currents are quietly different with the surface current. Since the semi-empirical model is based on the current observation around 5m layers, its predictions also disagreed with the trajectories.

In the condition of the wind blowing from the innermost to the entrance of the bay, drifting speeds of the 2 stations in the central area were larger than those in the inner area, so it is indicated that the

fetch of wind are concerned to the drifting speeds.

Concludingly, in order to improve the prediction, it is necessary that the vertical resolution of the model should be raised to know the detail of the current profile, especially in the surface layer. And the modelling of the unsteady process of the drifting by the variable winds considering the fetch will be necessary.

89. A Study for the Conservation of the Wetland Ecosystem: Establishment of the Method of Monitoring the Ecosystem and the Countermeasures to the Influence from the Surrounding Agricultural Lands.

(FY 1988-1992)

Fourth annual Report, Year of 1991.

Nature Conservation Bureau, Environment Agency

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A new vegetation map was used for trials in order to monitor the vegetational changes in the Kushiro mire.

Developments of *Alnus japonica* thickets were typically observed in the lower part of the main rivers, i.e. Kushiro River, Kuchoro River, Hororo River, and Setsuri River, on the vegetation map. Also, the areas of the typically high moor communities were dominated by *Sphagnum-Carex middendorffii* or *Oxycoccus quadripetalus* scattered on between the rivers.

Digitized geographic data, such as altitude, slope and direction of slope were overlayed on to these new vegetation data maps with the aid of a computer. Through the use of this computer system, typical geographic conditions and vegetation could be presented graphically.

Based on the floristic surveys dating back to 1988, 630 species of vascular plants from the Kushiro mire and its surrounding areas were catalogued. One thousand sheets of voucher specimens were gathered and are now in the care of the Botanic Gardens, Hokkaido University, and the Kushiro City Museum. There are estimated to be over 700 vascular plant species in the area of the mire.

A group of *Ranunculus* subgenus *Batrachium* species are expected to be a good indicator of lotic environment. A field survey in 1992 revealed 16 populations of these species among the 80 stations examined.

Flowering *Alnus japonica* was investigated at the two monitoring points in the Kushiro mire. The male and female flowers blossomed until September in the first year, and then flowered again in April of the second year. Pollination occurred between April and May, and then seed formation began. The number of spikes of male and female flowers at each shoot was investigated among three different trees.

Mammals were surveyed in the Kushiro mire and in the surrounding areas as well. *Apodemus speciosus*, *Mustela itatsi*, *Lepus timidus*, and *Cervus nippon* were discovered along the outskirts of the mire amongst the alder thickets.

A pair of White-tailed Eagle in this area tried to breed in the spring of 1991, but did not succeed. The White-tailed Eagle have failed to reproduce here, since 1989. Conversely, the largest number (43) of breeding pairs of the

Japanese Crane was counted in the spring of 1991.

Fish fauna was investigated at 16 sites along rivers where *Pungitius tymensis* was a characteristic species.

Caddis flies were collected from 29 sites and 41 species were identified.

The history of the surrounding river tributaries in the Kushiro mire have also been reported. At three stations along the tributaries of Kushiro River, the water level and the current of the river were also observed at 4 points within the mire. Depths of peat freeze were also measured throughout the winter season at several points with various types of vegetation.

A new numerical model of the heat balance near the ground was tested to monitor the environmental changes of the Kushiro mire. The data used in the model was mainly obtained from the routine meteorological observation in the Kushiro mire. The vertical profiles of calculated air temperature in and above the vegetation at night were approximately similar to the ones observed. The calculated heat balances near the ground show that the heat transfer to the ground is decreased with the reduction of water content of the top layer of soil, but that the latent and sensible heat transfers increase with it.

A specific focus of this landscape analysis was to identify how qualitative variables in photographs of simulated landscapes were significantly related to the evaluation of landscape of the Kushiro mire. This study was based on the data obtained from 96 subjects and 56 photographs taken at 6 viewpoints. Some patterns of relationships between landscape changes and evaluations of those were identified, and its conceptual and applied implication of the perceptual classifications were discussed. Another purpose of this study was to grasp the distribution and the movement of the eye fixations while inspecting sceneries. Eight scenes recorded on videotape from 5 viewpoints periphery of the Kushiro mire and 3 other viewpoints were presented to 12 undergraduate and graduate students. The distribution patterns of the eye fixations differed in respective scenes, but showed the tendency to concentrate to the edges of the landscape component such as river, lake and hillside.

90-1-(1) Prevention and Control of Wildlife Damage for crops
(FY1990-1994)

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1. Study on the Japanese monkey

The Japanese monkey (Macaca fuscata fuscata) lives in Honshu, Shikoku, and Kyushu. Damages of crops by monkeys have recently increased everywhere they live. This project is being conducted in Hakusan in Ishikawa prefecture, and Nikko in Tochigi prefecture, to study ecology and management techniques of the Japanese monkey for the purpose of prevention and control of the damage to crops.

(Hakusan region)

From July to September, the monkeys live in the sub-alpine zone above 1680 meters. Because the beech trees did not bear any nuts at all in the autumn of 1991, troops went down to seek foods at lower areas two months earlier than 1990.

We gathered information from old residents, about damages caused crops by the monkeys on dezukuri agriculture. Animals began to damage the crops, mainly Maize, soy, pumpkin and radish since the Taisho Era.

Monkey had been captured by hunters in Ishikawa and Gifu prefectures. Yakhata (slash and burn agriculture with shifting cultivation) was suited for the ecology of monkeys. This method increased the number of plant species because more were able to grow in the abandoned fields left after Yakhata. Therefore, more species of plants, such as vines and tall stemmed herbs, were available for the animal's consumption. Before Yakhata few species of plants were available.

The monkey's eating habits for fruits of Vitis and Actinidia was estimated by fecal analysis. Seeds of vine were found from September to November. Seeds of silver vine were found from half of the samples examined.

Three troops of monkeys were tracked from October, 1991 to February, 1992. The monkey's movement was strongly related to food availability, especially the presence of kaki fruits in near by villages. The total number of kaki fruits were counted at a village which was a wintering range of Taiko A1 troop to help to calculate their consumption.

In 1991 damages of crops occurred 3 months earlier than in 1990. The number of species damaged by increased from 10 to 19 species.

(Nikko region)

Five troops in three area were radio-tracked for the purpose of estimating home range of the troops. Home range was calculated by two methods, minimum convex polygon method and harmonic mean method. But the minimum convex polygon method was unsuitable to accurately calculate the ranges, because there are vacant areas which were not used by animals. Two troops along "Iroha-zaka" road had seasonal movement. In summer they used the lower sub-alpine zones. In winter they moved below 1300 meters. Winter core area in the home range of troops were narrower than their summer core area.

Damages to agricultural crops in Asio town was investigated by a questionnaire method. Damages to crops began in 1955. By 1975, 10 people reported damages caused by monkeys, 10 years later in 1985, the number of people reporting damages increased to 23. There was damage to 31 different kinds of crops, which included fruits trees, beans, grains, and various vegetables.

90-I-(2) Prevention and Control of Wildlife Damage for Crops

(FY 1990 ~ 1994)

Kazuhiro Yamase, Kazuhiko Maita, Masaaki Yoneda, Masato Nagatsu,
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1. Basic study

We conducted vegetation study with special reference to nut-production trees in Mt. Taihei study area (Akita prefecture) in 1991. Fagus crenata forest produces a large amount of nut, but the yearly production is not stable in this type forest. Nut-productivity of Quercus crispula is not so high as Fagus crenata, but Quercus crispula forest consists of more various trees that provide nuts and berries to the bears than Fagus crenata forest. In western Chuugoku Mountain study area (Hiroshima Prefecture), we analyzed and made maps of change of man made forest area from aerial photography. The man made forest area in 1947 was very small but the forest area increased in 1960's and 1970's in western Chuugoku Mountain study area. The increase of the man made forest caused decrease of capacity of forest for bears and shift of range from mountain area to lower area.

2. Study on nut-falling

The black bears in western Chuugoku Mountain study area depended on Kaki (Diospyros kaki) and Kuri (Castanea crenata) ripened on trees abandoned around villages in depopulated area as autumn food. We counted number of trees and studied fruit production of Kaki and Kuri in the study area. Sixty four percentage of kaki trees (n=102) and forty three percentage (n=136) of Kuri trees fruited in 1992 in the area. The production of the fruit related with chest height diameter and height of trees.

3. Radio tracking study

Three black bears were captured in 1992 added two bears studied from 1991, and attached with neck-transmitters for radio tracking study in western Chuugoku Mountains study area in Hiroshima Prefecture. The bears mainly use near village area and consume kaki fruits and kuri nuts in autumn. The bears spent much times in foot of mountain area in autumn, however denning sites located higher mountain area. One yearling of No.13 bear was captured in Mt. Taihei study area in April 1991, and attached a transmitter for study of mother-cub relationships. The yearling bear moved with mother in April and May then separated from mother bear in June 1991.

(FY 1990-1994)

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Results

1. Crane population in 1991-1992 winter.

In 1991-1992 winter, 4 species of cranes wintered in Izumi, Kagoshima: White-naped Crane, *Grus vipio*, Hooded Crane, *Grus monacha*, Eurasian Crane, *Grus grus*, and Sandhill Crane, *Grus canadensis*.

The results of count December, 1991, and January, 1992, are shown in Table 1.

Table 1. Number of wintering cranes

| Species | 16-18 December 1991 | 14-16 January 1992 |
|-------------------|---------------------|--------------------|
| White-naped Crane | 1,516 | 1,585 |
| Hooded Crane | 6,574 | 7,013 |
| Eurasian Crane | 2 | 1 * |
| Sandhill Crane | 3 | 3 |

Notes. (1) Several hybrids of Hooded and Eurasian Cranes are included in number of Hooded Cranes.

(2) One Eurasian Crane died on 3 January, 1992.

About 70 White-naped and 440 Hooded Cranes arrived at Izumi between the censuses of December and January. Wintering population in 1991-1992 reached the largest number on the middle of January, in like cases of the past years.

Furthermore, we could find at least 51 White-naped and 3 Hooded Cranes arriving at roost pond in Izumi during the morning of 19 January, 1992. It seemed that these cranes have stayed somewhere in Korea and migrated to Izumi by hit prevailing cold wave.

So the whole wintering population in 1991-1992 was 8,660: 1,640 White-naped Cranes and 7,020 Hooded Cranes.

2. Number of the cranes in the Outer area in the daytime.

Table 2 gives the number of cranes which lived in the Outer area in the daytime of the middle of January, 1992.

Table 2. Number of cranes in the daytime in the Outer area on 12-13 January, 1992.

| Species | Akune district | Izumi district | Total |
|-------------------|----------------|----------------|-------|
| White-naped Crane | 4 | 82 | 86 |
| Hooded Crane | 55 | 730 | 785 |

Only 59 White-naped Cranes, 785 Hooded Cranes, and total 871 cranes (10 percent of 8,602, see Table 1) lived in the Outer area. The number of cranes in the Outer area remarkably decreased, partly because an area of small crane-roost in Akune district has been destroyed and most of Akune farmers began to chase the cranes under the policy of Akune City, and partly because environment of some areas in Izumi district made a change to worse.

3. Feeding behaviour of cranes.

All cranes wintering in Izumi and Akune district inhabit the cultivated lands, and it is clear that numerous and most important area for wintering cranes are rice field unused in this season.

Composition of cultivated land in the Central area was mapped. 14 study areas were set in the Central and Outer areas. For the purpose of research of feeding behaviour of the cranes in the field other than rice field, these study areas were selected in the field of vegetables or beer wheat, and rice field adjacent to the field of vegetables.

Research was made on 21-25 December, 1991, and 20 January to 16 February, 1992 ; a total time of the research was 112 hours and good data were produced from observations of 88 hours ; 76 hours for the Hooded cranes (5 adult males, 5 adult females, and 3 juveniles; 18 observations in 16 areas in the Central and 2 areas in the Outer areas), and 12 hours for the White-naped Cranes (1 adult male, and 2 adult females ; 3 observations in the Central and 1 area in the Outer areas).

From these observations the following results were obtained.

- (1) The cranes did not damage the vegetables in the least degree. In fact, there were no cranes settled in the field of vegetables, and the crane seldom intruded into this field.
- (2) Some cranes were feeding beer wheat, but it seemed that the cranes did not eat the grass of beer wheat, and that beer wheat field was not damaged by the wintering cranes.
- (3) Usually the cranes fed on very small articles, and the component of their natural food was not analyzed through the field observations.
- (4) The inquiry about the distribution of cranes in western and central Japan has been made from 1985 annually.

Fundamental and interest data were obtained. Most important fact is that Tushima and Iki Islands are the refuge on the way to northern breeding areas.

90-III Prevention and Control of Wildlife Damage for Crops

(FY 1991 - 1995)

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A. Population management of birds in crop lands

Some birds such as crows, gray starlings, turtle doves and bulbuls cause damage to crops. At the same time, these birds take insects as food, suppressing the increase of insect pests. Therefore, we need to manage the populations of these birds both to reduce crop damage and to suppress the occurrence of insect pests. For this purpose it is crucial to estimate the crop damage caused by these birds, the role of them as predators on insect pests, and population densities and movements of the birds as exactly as possible.

1. We could estimate accurately the percentage of fruits damaged by birds by sampling fruits systematically from all parts of a tree. Because damaged plants were aggregated in edges of a field in cases of sprouting soybeans and corns, it was necessary to divide a field into two parts to obtain an accurate estimate.

2. Gray starlings, Sturnus cineraceus, which were caught around pear orchards, showed that they ate many insects including pest species of pears. Especially, young birds preferred to prey on adult cicadas, Graptopsaltria nigrofuscata. We found that population density of the tent caterpillar, Malacosoma neustria testacea, was stable in recent years, suggesting that predation by birds played some role.

3. Marine radars were used for observing land bird movements because of the low cost and ease of operation. To eliminate ground or sea clutter obscuring the track of the bird on the radar screen, the antenna was remodelled and topographic effects were utilized by locating the radars behind a raised bank or in a pit. This technique allowed us to remove between 20% and 100% of the sea and ground clutter depending on conditions.

4. Numbers of four bird species typical in cultivated areas were censused monthly along five routes, about 4 km long each, from January 1991 to March 1992. The total number of birds fluctuated

tuated differently in each study area, perhaps because of habitat differences. The density of the rufous turtle doves, Streptopelia orientalis, remained stable. Gray starlings were plentiful in the summer but decreased quickly in the fall. Brown-eared bulbuls, Hypsipetes amaurotis, increased in October but decreased in the breeding season. With the exception of gray starlings, most birds spent the majority of their time in shelterbelts rather than in cultivated land. Starlings were often observed to eat insects in cultivated areas.

5. Ural owls, Strix uralensis, caught more forest floor animals when *Sasa* shrubs in the secondary forests were cut. This fact suggests the necessity of forest floor management to assist in the settlement of Ural owl in rural forests.

B. Population management of the black woodpecker and other birds in buna forest

The black woodpecker, Dryocopus martini, is an endangered species in Japan. As part of an effort to prevent its extinction, we censused the woodpeckers' density and distribution. The avifauna in buna (Fagus crenata) forests and the effect of avian predation on insects were also examined to collect data necessary for conserving buna forests where black woodpeckers live. Analysis of avian carrying capacities and the effects of treatments on it will allow us to develop a more effective strategy for managing the bird populations in these forests.

1. In 1991 we observed the breeding of the black woodpeckers in four regions of the Tohoku district, all of them from the buna zone of Aomori Prefecture. The field signs of the bird were recorded only in the northern part of Tohoku district.

2. Analysis of the droppings of black woodpeckers revealed that their food in early spring consisted of Scolytid beetles, Cerambycid beetles (Psephactus remigar), ants (Lasius niger), and other arthropods. In early summer, food was mainly adult beetles walking on the tree trunks.

3. The composition of the breeding bird community in buna forest at Mt. Hiuch varied depending on the altitude. The composition and the density of breeding bird community in the buna forest of Mt. Hakkouda showed no difference between 1990 and 1991.

4. The population of buna caterpillars, Quadricalcarifera punctatella, were in a decreasing stage after a climax in Mt. Hakkouda region. At the same time the percentage share of the caterpillar in the content of nestling food in July decreased markedly compared with the previous year.

5. Dead trees are used as feeding sites by woodpeckers. Most of the dead trees at the study site were derived from broken trees after decay caused by fungi infestation. The density of dead trees on which feeding marks by black woodpeckers were observed was 0.6 per ha.

6. The structure of the buna forest was investigated at the upper stream region of the Isawa river. A buna forest on the land slide area showed an even aged stand, and the distribution pattern of DBH showed a normal curve. A spatial distribution of the population showed a random pattern of small contagious groups of individual trees.

91. Occurrence Mechanism and Prevention of Soil Loss into the Sea from
the Agricultural Land in Ryukyu Islands
(FY 1991-1995)

Ministry of Agriculture, Forestry and Fisheries

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Recently, it became clear that marine ecosystem started to be affected by the soil loss of erodible soil and change of agricultural environment in Ryukyu Islands. This situation made us haste to develop effective management systems.

The objective of this study was to develop a systematic technique to conserve and maintain marine ecosystem on reasonable cost in cooperation with research institutes under the Ministry of Agriculture, forestry and Fisheries and the Ministry of Construction.

The first year's results are summarized as follows.

1. Non-woven fabric as a covering material and *Lolium multiflorum* Lam as a cover crop were effective for the prevention of the soil loss.
2. Three tropical leguminous species, i.e. *Cajanus cajan* and *Glycin max* were found as effective species for the prevention of soil loss.
3. The deep tillage treatment reduced surface runoff water through increasing percolation water and consequently the soil loss was reduced.

4. The saturated water capacity of A layer of surface gleyed red and yellow soil is small at the cutting forest area. Therefore, it is easy to occur the erosion by the surface runoff water.

5. The surface charge characteristics of typical soils in Ryukyu Islands were investigated with surface chemical view of soil. The surface charge value of Acid red-yellow soil showed to be minimum.

6. The subsoiling by the subsoiler with vibrating L type blades was effective for the improvement of infiltration capacity of the soil which reduced the soil loss in the sugar cane (*Saccharum officinarum* L.) field.

7. The leaf mold treatment and the treatment using the residue from the accumulated 2 cm FH layer of broad leaf forest were effective for the prevention of soil loss under experimental condition.

8. Poly vinyl alcohol treatment and compost incorporation to 20 cm depth treatment were effective for the promotion of soil aggregation. And the hardpan breaking by power shovel improved the saturation permeability.

9. A model was developed to simulate the water balance in Acid red-yellow soil. The model can simulate water movement which is closely connected with the soil loss. The deviation of predicted values by model from the measured one for water retention in the surface horizon were less than 10%.

10. The soil particle of Acid red-yellow soil in runoff water was classified as fine textured soil and it occupied high percentage in the turbidity and was distributed uniformly in the cross section of the supercritical flow.

11. The rainfall runoff model was developed for analysis of function of the reservoir for water recycling in the Acid red-yellow soil area. And the runoff percentage and the maximum time lag of runoff was estimated using this model.

12. The trap efficiency against turbidity by the filter method was found to be 30%. And the gradation and sedimentation rate of the soil particles were determined in the river at Acid red-yellow soil area.

92. Diffusion Process and Monitoring Method of Pollutants
related to High Technology Industries

1. Studies on the pollutants in the atmosphere and
in the groundwater
(FY 1988-1992)

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1. Objectives of the study

Due to recent rapid increase of high technology industries, the environmental impact by new chemical substances has become of great social concern. However, the behaviour of those chemicals in environment, such as emission condition, diffusion process in atmosphere, in soil, in ground water, etc. are still unknown. This project aims to clarify the transport and diffusion of the chemicals released from high technology industries through field and laboratory experiments, and to propose practical simulation models of these chemicals in environment. This project consists of the following sub-themes:

- ① modeling of the diffusion process for inland area with complex terrain.
- ② improvement of the diffusion model for inland area with complex terrain.
- ③ modeling of the deposition of chemicals on the ground and water surface.
- ④ modeling of the diffusion of chemicals in underground water.

In this fiscal year, a field experiment for atmospheric environment was executed in northern part of Kanto plain in July. The major purposes of the experiment were the airflow structure in a shallow valley and atmospheric environment.

The field experiment of movement of chemicals in water phase was

conducted in a irrigation channel in the same area two times on October 1991 and February 1992.

2. Airflow structure and the atmospheric environment

In the atmospheric studies, two kinds of observations were done. One is the study of diffusion field, ie. the meteorological components. The other is the concentration distribution and the diurnal change of chemical components.

In the meteorological experiment, vertical profiles of wind velocity and temperature were measured by pilot balloon and radio sonde soundings. The chemical substances were sampled by micropumps to absorbent and analysed by gas-chromatography in laboratory. The gas sampling were done fourteen times at ten points scattered in a area of about 20km x 20km.

The meteorological observation showed that the objective area is quite low wind area. The sea breeze from Tokyo Bay reaches the area not every day and if arrives there it is late afternoon. Therefore the low wind or nearly calm condition continues from morning to late afternoon, and diffusion of airborne chemicals is not rapid in the area.

The concentration distribution of chemicals in the area were relatively wide. The differences of the concentration by points were not large comparing to the observation in a industrial park last year. The difference will be attributable to the difference of the emission and also diffusion field. The area is wide shallow valley and many emission sources are scattered in the area.

The diurnal change of concentrations were also typical as the low level sources in low wind condition. The concentration was high in morning hours, decreased to late morning to early afternoon and increased from evening to night.

3. Groundwater pollution caused by infiltration of polluted river water

One of the reasons of groundwater pollution is considered the infiltration of polluted river water into the ground water. This effect is important to contribute to the background concentration of groundwater even if it is relatively low.

Field studies were made at the alluvial fan formed in the inland basin on October, 1991 and February, 1992. In this district, three factories which use trichloroethylene and discharge those waste waters to the irrigation water channel. Waste waters from two factories were discharged to the upstream branch channel having the narrow width and then discharge

to the main irrigation channel. This main channel flows through a natural river bed at the downstream of some hundred meters.

In the middle point, the third factory's waste water discharges to the main irrigation channel. This channel has the characteristics that there are many artificial fall having almost 50 cm height. In this area, the polluted river water is seemed to infiltrate into the groundwater and cause the groundwater pollution. To investigate the infiltration mechanism, it is important to reveal the relation between river and groundwater.

On October, this channel had large river discharge and so the polluted water flew rapidly. For that reason, a little decay of trichloroethylene was ascertained. A relatively large decay of it occurred at the artificial fall for the strong mixing. On February, this channel had small river discharge and so the polluted water flew slowly. And also, the height of the artificial fall became large and the strong decay of trichloroethylene occurred. There are strong relations between the height of the artificial fall and the residual percentage of the downstream to the upstream at that point more than about 30 cm height.

2. Clarification of Behavior of Pollutants and Prevention for
Extention of Them in Groundwater in Deep Layers
(FY 1988-1992)

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Geological Survey of Japan (GSJ)

Agency of Industrial Science and Technology

Ministry of International Trade and Industry

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When widespread groundwater pollution has to be considered, one of the most important factors controlling groundwater movement is to know whether the geologic strata is continuous or not. In the study, four observation wells have been drilled in Honjo, Saitama Prefecture. Based on those borings, a 250-m-deep well was drilled at Kazo, Saitama Prefecture to examine the continuity of the geologic strata from the northwestern to the central part of the Kanto Plain. The authors also tried to make clear the geologic structure of the study area by physical prospectings next to the Kazo boring site.

In the laboratory, the authors examined how groundwater moves under the condition of occurrence of density flow, using a sand box model. The sand box was composed of five aquifer-aquiclude layers and was analysed by thermography.

On the other hand, they examined whether groundwater flow exists from one aquifer to others through the well casing itself or not at a multi-screened well.

The following results were obtained through the surveys of the fiscal year 1991.

1) Core samples were obtained at every depth from the 250m-deep-well at Kazo, Saitama Prefecture. From the inspection of all the core samples, it can be pointed out that a unit of gravel, mud, and sand deposits repeatedly.

from the lower layer to the ground surface.

2) Next to the boring site, seismic and VSP prospectings were made. A combination of both methods is valid for prospection of geologic structure related to groundwater flow. The result of the prospections shows that the deposits having a good continuity are stratifiedly distributed, but some possibility of existence of a fault occurs. The boring site is located near the steep inclined lines of chloride concentration of groundwater bearing about 200 m below the ground surface as shown in Fig. 2.8. There is some possibility that the fault playing a role as barriers for lateral groundwater movement made, such a clear difference of water quality.

3) From analysis of the images by thermography at the sand box model experiment, it is found that newly introducing cold water into an unconfined groundwater body laterally flows quickly and selectively near the groundwater table in spite of its heavy specific gravity. The cold water does not diffuse widely in upper aquifers, and even if there exists some withdrawing well, groundwater in upper aquifers do not go down into lower aquifers, if there is no movement of groundwater in lower aquifers.

4) Continuous pumping from each screen at the multi-screened well was done using packers to extract groundwater only from the aquifer that the screen was set. After taking off the borehole pump, groundwater flow from one screen to others was certified to exist passing through the well itself as a by-pass through the inspection by borehole TV camera. The vertical groundwater flow through the well was also confirmed both by the temperature and the electric conductivity loggings. This vertical flow has an important meaning when pumping is stopped for a long time. That is, when groundwater having higher potential head (in general, shallower groundwater) has been polluted, the vertical flow leads to deeper groundwater pollution.

There are many abandoned wells because of bad water quality caused by pollutants. If groundwater pollution in deeper aquifers is spreading through the by-pass of the well itself, it is urgently necessary to take countermeasures; such as complete stopping up the well, injecting cement milk to prevent the spreading of pollutants to deeper aquifers.

3. Fates of Chlorinated Hydrocarbons and Rare Metals
in Agro-Environment
(FY 1988-1992)

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Hiroyuki Kawashima, Takeo Masuda, Takayuki Suzuki,
Shigeyoshi Gotoh, Takayuki Saitoh, Shigemitsu Arai,
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Ministry of Agriculture, Forestry and Fisheries

Behavior of volatile chlorinated hydrocarbons and several rare metals in agro-environment and their effects on biological functions were studied. Results obtained in 1991 were summarized as follows.

1. Photodegradation, plant absorption and animal tissue transfer of volatile chlorinated hydrocarbons.

Photodegradation of trichloroethylene (TCE) and tetrachloroethylene (PCE) and 1,1,1-trichloroethane (MCF) in distilled water by irradiation with UV-light was $PCE > TCE > MCF$ and it was accelerated by adding 0.2 % acetone as photosensitizer, even at 305 nm.

The absorption and discharge of PCE from the plant leaf surface was determined by using an equipment made on an experimental basis. After the exposure to PCE in the equipment, the plants were taken out and analyzed immediately. The maximum concentration of PCE in the plants was not higher than the concentration in the air. The data obtained from the absorption process were evaluated according to the model of the two-compartment first-order reaction. In the decline curve of the residue concentration in the plants, the model of the first-order reaction gave the good fit.

Survey on the contamination of agricultural environment with TCE, PCE and MCF around a chemical factory at three points and three times was made. The maximum concentration of river water in ppb was 162 of TCE, 6.9 of PCE, and 57 of MCF.

Transfer of the three chlorinated compounds including the metabolites to the blood and the internal organs at 3.5 hrs. after their oral administration was TCE > PCE > MCF with nursing kids.

2. Behavior of rare metals in soils and waters and their effects on biological functions.

Gallium did not have toxic effect on the growth of rice seedlings until Ga concentration in culture solution reached at 10 ppm. However, there appeared a drastic retardation of the plant growth in the Ga concentration between 10 and 25 ppm. The Ga concentration in the rice seedlings increased rapidly as Ga concentration increased in the culture solution. These results, in combination with last year's study, indicate that Ga has rather mild toxic effect on the rice plants as compared to Be.

The concentrations of toxic inorganic elements in the river water samples collected from various parts of Japan were generally very low with the values below ppb levels. Even Zn, commonly having the highest concentrations relative to other elements, showed quite low values below as low as 10 ppb. The lowest concentration detected in the river water was found to be 0.X ppt for Pb. The concentrations of the elements in the course of this study were very wide in ranges and distributed at least over three orders of magnitude.

The effect of added V with different valencies (III, IV, V) on the top growth of carrot was low and indicated statistically insignificant difference from the control treatment with no added V, with the exception of V 10 treatment (treated soil V content 10 times greater than natural background V level). Similar trend was observed for root growth of the carrot related to V treatments. When six elements (Be, V, Ga, La, Sb, Bi) were added to the soil, concentrations of those elements in the plant top increased apparently for La, slightly for Be, V, and Ga, and little for Sb and Bi.

The decrease in grass yield due to V application was the greatest in the 1st harvest and then the trend lowered gradually in the subsequent harvests from 2nd to 5th harvests. The V concentration ratios in the top to root were considerably high and scatter from 20 to 300, and the ratio decreased with increased V applications. These results suggest that the applied V apparently inhibit the growth of the grass, especially in the early stage of the growth. Accumulation of V from the applied V was more marked in the root parts than in the top parts. There was an increased V accumulation in the grass top with increased V application.

Using newly devised hen's egg embryo culture system, LD50 of V(IV) and V(V) was found to be 0.55 and 0.8 μmol , respectively. Deferroxamine was most excellent detoxicant working as a V absorption inhibitor. Dose of V(V) to hamster tested promoted a vitamin E deficiency, and V(IV) brought about lipid peroxidation to be a hemolysis factor in vitro.

4. Development of Monitoring Method of Biological Samples to Assess Exposure to Pollutants from High Technology Industries (FY 1988-1992)

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National Institute of Public Health

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National Institute of Hygienic Sciences

With a view to prevent environmental pollution by chemicals discharged from high technology industry, the Environmental Agency launched a study project in 1988 for studying the measurement methods of pollutants discharged from the high technology plants, their behavior in the ambient air, soil and groundwater, their movements in agroenvironment and methods of evaluation in human body, and developing a comprehensive environmental monitoring method. Our group was assigned to develop analytical method of human samples to monitor exposures to volatile chlorinated hydrocarbons, to observe their movements in humans, and to study their behavior in foodstuff which are considered the primary source for exposure and their analytical methods.

Many volatile chlorinated hydrocarbons are used in the high technology industry, and groundwater contamination by these compounds is being reported to pose grave problems in the society. There are many reports on the analytical methods of these compounds in the water and in the air, and GC with ECD which is usually employed for organic chloride analyses is most frequently used. There are, however, very few reports on the analysis of human samples. These compounds are estimated to be present at low concentration in the human samples.

It has been considered that much of chlorinated hydrocarbons such as trichloroethylene and 1,1,1-trichloroethane ingested into the human body is metabolized and excreted in the urine mainly as trichloroethanol and trichloroacetate. In order to know the extent of the exposure of peoples to these compounds, the urinary concentration of trichloroacetate (TCA), one of its main metabolites, has been suggested as an index of volatile chlorinated hydrocarbons exposure. The spectrophotometric method based on the development of deep red color in a boiling mixture of pyridine and strong alkali as Fujiwara reaction has widely used for monitoring the extent

of exposure in industry hygiene. But this spectrophotometric method has not sensitivity enough to determine TCA in the urine who lives in usual environment. It has been required to determine the trace levels of TCA in urine as total amount of trichloro-compounds. The spectrophotometric method based on the development of deep red color in a boiling mixture of pyridine and strong alkali as Fujiwara reaction has widely used for monitoring the extent of exposure in industry hygiene. But this spectrophotometric method has not sensitivity enough to determine TCA in the urine who lives in usual environment. So we researched and developed the simple method with a high sensitivity using up-to-dated technology. In the previous studies, attempts of flow injection analysis based on the Fujiwara reaction, and ion chromatography using a conductivity detector have applied for measurement of urinary TCA. However their sensitivity and utilization was not enough in practical.

In this year, two methods using gas chromatography with electron-capture detector (ECD-GC) and capillary electrophoresis were investigated to develop the furthermore improved quantitative trace analysis of TCA. TCA after esterification with diazomethane or after conversion to the volatile chloroform as the thermal decarboxylation product of TCA in the injection port of GC was quantitated in urine by using capillary column. The clean-up procedure was studied by using Sep-Pak tC18 cartridge, that was combined with ether extraction method. The method with thermal decarboxylation of TCA is attractive because the procedure is simple, the column is less contaminated and a rapid quantitation is possible. The sensitivity ($0.3 \mu\text{M}$) makes it suitable to estimate normal exposure to trichloroethylene and other chlorinated hydrocarbons in human samples.

A simple and rapid method for the determination of volatile chlorinated organic compounds in foods was developed by the use of head-space method with the addition of a standard solution. Ten grams of samples were mixed with 90 ml pH7.0 phosphate buffer, transferred to 120 ml vial for head-space analysis added with 0.2 g ascorbic acid and 10 μl standard solution or methanol, stoppered the vial tightly, shaken for 5 min and kept for 2 hr. Two hundred μl of head-space gas of the vial was subjected to analysis by ECD-GC. The limits of determination were between 0.1 and 0.5 ppb for 6 kinds of volatile chlorinated organic compounds. It seems that there are two ways in the contamination of foods by volatile chlorinated organic compounds, that is, one by use of contaminated water and the other transferred to the foods from polluted air.

APPENDIX List of the Research Institutes Concerned

The ministries and agencies concerned are:

NAP National Police Agency
HDA Hokkaido Development Agency
STA Science and Technology Agency
EA Environment Agency
MF Ministry of Finance
ME Ministry of Education
MHW Ministry of Health and Welfare
MAFF Ministry of Agriculture, Forestry and Fisheries
MITI Ministry of International Trade and Industry
MT Ministry of transport
MPT Ministry of Posts and Telecommunications
ML Ministry of Labor
MC Ministry of Construction

- END -

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